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SO2 Free Two-Stage Coal Combustion Process

Appendices

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SO_2 FREE TWO-STAGE COAL COMBUSTION PROCESS
APPENDICES

by

Applied Technology Corporation
135 Delta Drive
Pittsburgh, Pennsylvania 15238

for the

ENVIRONMENTAL PROTECTION AGENCY

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The volume contains the appendices to the report entitled, "SO_2 Free Two-Stage Coal Combustion Process Progress Report". Appendix A is a discussion of the experimental combustor design, construction, and operation. Appendix B details the laboratory work conducted for this study. In Appendix C is presented the Two-Stage Coal Combustion Process simulation and economic evaluation.

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EPA Project Officer

Mr. Douglas A. Kemnitz, of the Control Systems Laboratory Division was the EPA project officer for the work discussed in this report. Mr. Stanley J. Bunas is the EPA project officer for the continuation of this work.

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APPENDIX A
COMBUSTOR DESIGN, CONSTRUCTION, AND OPERATION

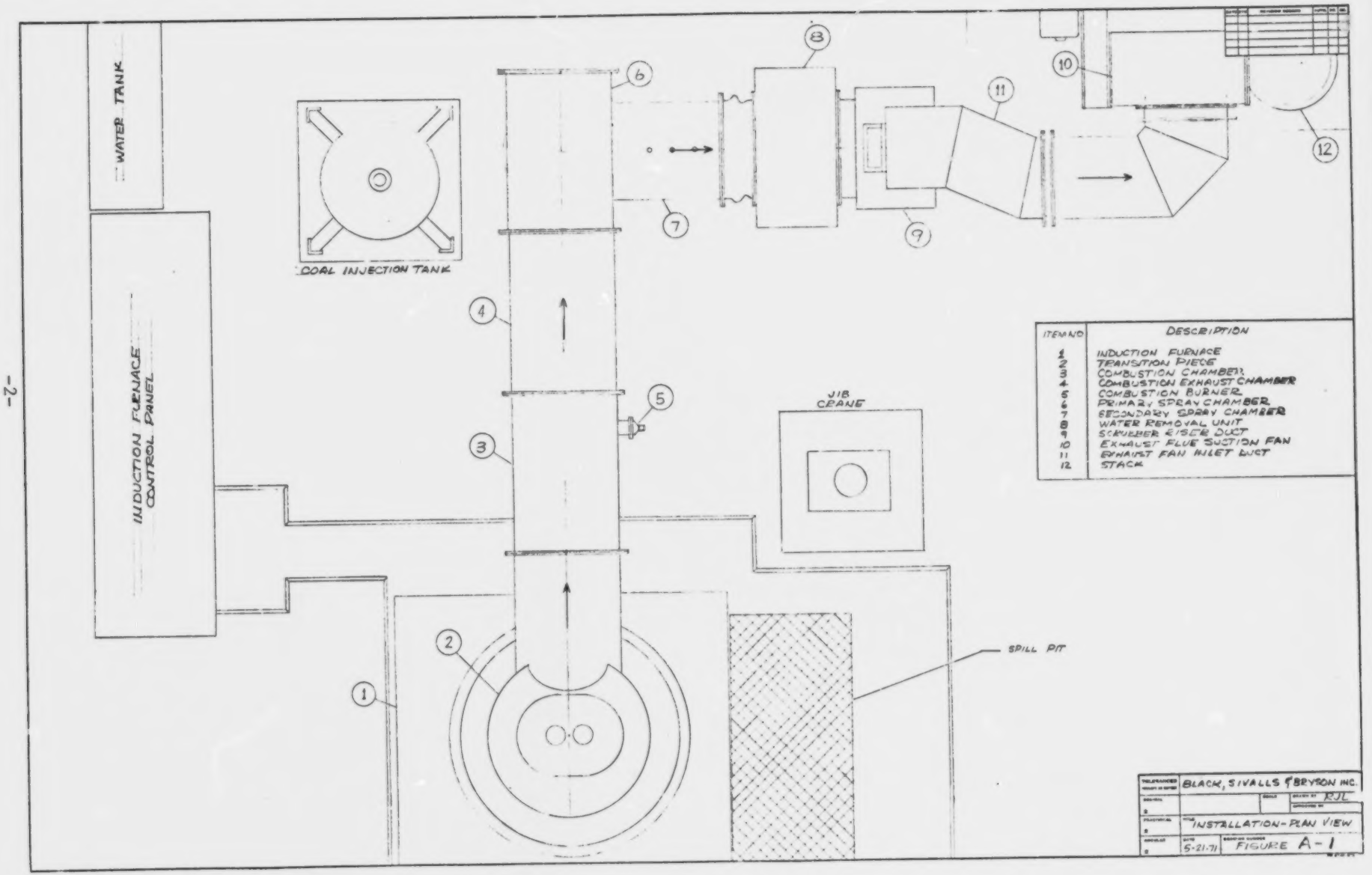
The following is a discussion of the design, construction, and operation of the experimental combustor system in which an induction melting furnace was used to simulate the combustor and an offgas processing system was incorporated to prepare the combustor offgas for release to the atmosphere. The coal injection system, process instrumentation, and controls, sampling, and requisite auxiliary equipment will be discussed.

Experimental Combustor System

An installation plan view of the experimental combustor system is shown in Figure A-1. The installation was constructed on three levels. The induction melting furnace was positioned on the lowest level in a firebrick-lined pit and the furnace control panel, coal injection system, and offgas processing system were located on the second or main operating level. An emergency spill cavity was constructed in the pit to capture molten metal if a furnace run-through or an emergency pour should occur. A two-ton (capacity) jib crane was located on the main operating level to move equipment and iron ladles. An induced draft fan was located on the third or uppermost level to maintain negative pressure on the experimental combustor process system. The entire operating area was enclosed with a firewall and a roof-mounted ventilating fan was installed for rapid removal of unwanted gases.

An induction melting furnace was selected to simulate the combustor because it is a convenient means of preparing a molten iron bath and maintaining it at a specified operating temperature. The induction furnace was designed to prepare a three ton molten bath in four or five hours. Whenever it is desired to remove the contents of the induction furnace, the furnace is disconnected from the rest of the system, tilted, and the molten metal poured into a ladle for casting into small pig molds or large starter block molds. The iron pigs and starter blocks are reused in the furnace.

The combustor offgas contains carbon monoxide and hydrogen in addition to other constituents. Therefore, prior to atmospheric elimination, the gas is burned to carbon dioxide and water, cooled, and scrubbed. This is accomplished in the offgas processing system shown in Figure A-1. The combustor (1) is connected to the offgas handling system using a gas-tight transition section (2) mounted on top of the furnace. The design of this piece of equipment is such that a gas-tight seal could be made with the induction furnace while the total surface area was minimized to limit radiant heat loss. The latter consideration necessitated the redesign and fabrication of a second transition section when the



ITEM NO	DESCRIPTION
1	INDUCTION FURNACE
2	TRANSITION PIECE
3	COMBUSTION CHAMBER
4	COMBUSTION EXHAUST CHAMBER
5	COMBUSTION BURNER
6	PRIMARY SPRAY CHAMBER
7	SECONDARY SPRAY CHAMBER
8	WATER REMOVAL UNIT
9	SCRUBBER EXCEL DUCT
10	EXHAUST FLUE SUCTION FAN
11	EXHAUST FAN INLET DUCT
12	STACK

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INSTALLATION - PLAN VIEW

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FIGURE A-1

excessive heat loss resulting from the initial design led to slag crusting problems which caused operational difficulties. The transition section (which also provides support for coal and air injection and sampling equipment) directs the combustor offgas into a flare section (3) for complete combustion to carbon dioxide and water. Air is injected into the flare section which contains a natural gas pilot burner (5) as an igniter for the gas-air mixture. Complete combustion of the offgas occurs in the second flare section (4).

The offgas from the flare flows to a quench section (6) where it is cooled by contact with water sprays. The water-saturated gas stream enters a wetting section (7) where it undergoes further water cooling (provided by radially mounted sprays) to remove large-sized particulate matter (if any). The cooling water is separated from the saturated gas stream in the dewatering section (8). The scrubber section (9) located downstream of the dewatering section (8), removes any particulate matter which may be present in the offgas. The clean gas exits the scrubber section into draft fan (10) and is eliminated from the system through the stack (12). The draft fan maintains negative pressure throughout the combustor system and discharges the cooled and scrubbed gaseous products of combustion to the atmosphere.

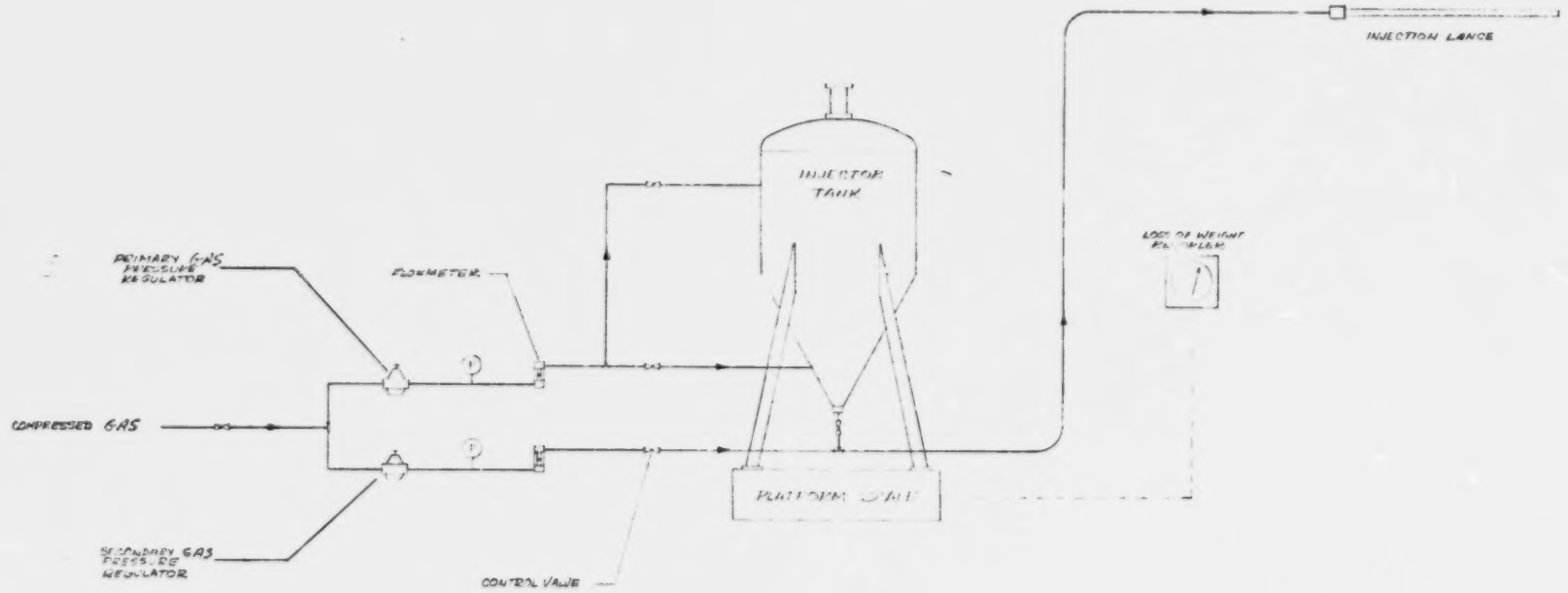
The transition and flare sections were lined with high alumina castable refractory designed to withstand a 2800-3000°F combusted offgas temperature and yield a 400°F outer steel shell temperature. The temperature of gas leaving the quench section was controlled in the range 150-200°F; hence, a refractory lining was not used for downstream equipment.

Injection System

The pneumatic injection system is shown in Figure A-2. To minimize the transport gas requirements, a dense-phase pneumatic system was selected. In such a system, material is fed batchwise into an injection tank, pressurized and fluidized using part of the transport gas. The material is subsequently conveyed out of the tank via a hose to the injection lance.

Additional (secondary) transport gas is added at the tank exit to the hose to insure adequate transport velocity and to balance pressure drops. The material injection blow tank was located on a weight scale with a loss-of-weight recorder. During injection, an instantaneous weight can be obtained from the scale dial and a permanent loss-of-weight record for the entire run is obtained from the recorder.

The pneumatic injection system is used to inject several materials into the molten bath. Graphite and several coals were injected using the system to determine solubility and gasification rates. Slags are synthesized by injecting the requisite ingredients beneath the metal bath. The materials dissolve as they float to the surface where the fluid slag collects to the desired height.



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DENSE PHASE PNEUMATIC COAL INJECTION SYSTEM

FIGURE A-2

Injection Lances

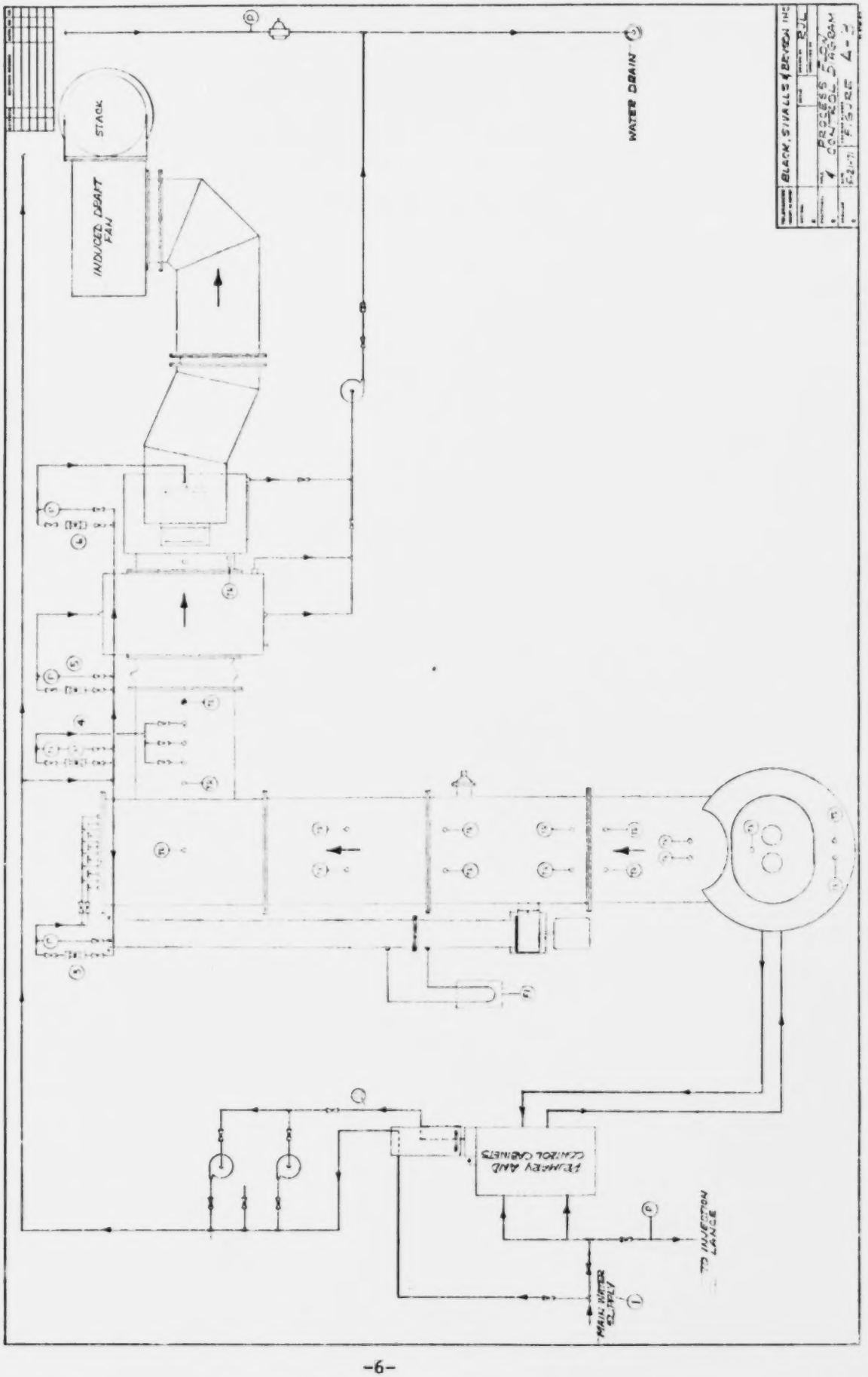
To a large extent, the successful operation of the experimental combustor depends on suitable injection lances. Since both solids and air are injected beneath the molten iron, a submergible lance is required. Two types of non-cooled lances were used--graphite fluxing tubes and refractory or ceramic coated lances. The graphite fluxing tubes were found to be better suited to submerged injection and were used almost exclusively. Unlike the ceramic coated lances which were prone to thermal shock failure, or refractory coated lances which were prone to slag attack (chemical reaction) failure, the graphite fluxing tubes showed adequate useful life for our purposes. This useful life was limited only by the graphite dissolving in the molten iron bath or reacting with the air flowing through the lance.

For extended experimental and commercial life, internally-cooled metal lances should be used. In coal injection applications, the internal cooling also offers additional protection against the possibility of coking the coal within the lance--which would plug the lance. Water cooled lances are currently used above molten iron in basic oxygen steel refining. However, it is known that the introduction of water into molten iron can present serious safety hazards. Even though safety features can be incorporated within the lance design to minimize these hazards, the need for a totally fool-proof system in power plant applications is paramount to maintain reliable and constant operations.

An experimental study is now being conducted to design and evaluate a non-aqueous cooled submergible lance system for both experimental and commercial combustor operations. Typical non-aqueous cooling fluids such as oils, molten salts, and low-melting point alloys could be used which, in general, eliminate explosive possibilities because they do not generate large amounts of gases capable of instantaneous expansion. Oils are intrinsically safe because the coking and cracking that occurs at the high temperatures involved produce only small amounts of gases that under typical expected combustor operation should not generate an explosive condition. Molten salts may create problems. Nevertheless, they are suitable as cooling agents insofar as they will prevent an explosive condition. Probably the most desirable cooling agents are low melting point metals or alloys. Alkaline metals, such as sodium, vaporize when exposed to molten iron and will subsequently react with atmospheric oxygen or water vapor. Much more suitable are the low-melting-point, high-boiling-point alloys such as lead-bismuth eutectic which will safely remain in the iron if leaked into the molten bath. These materials, operating in a closed-loop cooling and heat exchange system offer much promise for a lance system.

Process Instrumentation and Control System

The design of the experimental combustor process instrumentation and control system is shown in Figure A-3. The system does not include the coal injection system which is treated separately.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PROCESS FLOW
CONTROL DIAGRAM
FIGURE 4-2
WATER DRAIN
STACK
INDUCED DRAFT FAN
TO INCINERATOR
MAIN WATER SUPPLY

Process water is taken directly from the local water supply main (1) and used first to cool the induction furnace and its power supply. It exits (2) at temperatures in the range of 90-100°F which are suitable for cooling and scrubbing the offgas. The water exiting the furnace power supply panel is used for the evaporative cooling of combusted offgas in the quench section (3), in the wetting section (4), in cooling of the internal baffle of the dewatering section (5) and for scrubbing any particulates from the gas in the wet scrubber (6). Water flow rates are measured with rotameters using an integrating meter as a check. Process temperatures are measured at the points marked "T", on four potentiometric recorders. All high-temperature gas streams are monitored with platinum 13 percent rhodium thermocouples, and low temperature gas and water streams are monitored with copper-constantan thermocouples. Gas flow measurements of the combustion air injected into the flare section and the total offgas stream in the reduced draft fan are determined using orifice meters.

Raw Materials and Supplies

Raw materials used for experimentation are: iron, slag ingredients, sulfur, air and nitrogen. Iron was purchased in pig form and had the typical composition shown in Table I-A. The slag materials were lime, calcium sulfide, sulfur, silicon, and alumina. The oxides were purchased from refractory suppliers to minimize contaminants without going to the cost of purchasing reagent grade materials.

In this study, several coals and graphite of the compositions shown on Table II-A were used. The air and nitrogen were received via tank trailer. The trailers were connected to an outside station from which various streams were piped to the system where required.

Solids injection beneath the molten bath was effected through graphite "fluxing tubes".

TABLE I-A

TYPICAL PIG IRON COMPOSITION

Carbon	4.37
Silicon	1.17
Sulfur	.026
Phosphorous	.085
Manganese	.93

TABLE II-A

COALS USED IN EXPERIMENTATION

	Stillwater Coal	Consol Sea Coal	Bureau of Mines -1/4" Coal	Bureau of Mines -1/8" Coal	Bureau of Mines -1/16" Coal
Proximate Analysis					
Moisture	2.0%	1.9%	1.9%	1.9%	1.9%
Volatile Matter	38.4	38.8	34.0	34.0	34.0
Fixed Carbon	45.1	54.1	51.3	51.3	51.3
Ash	14.5	5.2	12.8	12.8	12.8
	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis					
Hydrogen	5.1	5.5	4.9	4.9	4.9
Carbon	67.8	79.0	72.2	72.2	72.2
Nitrogen	1.0	1.6	1.5	1.5	1.5
Oxygen	8.2	7.1	7.1	7.1	7.1
Sulfur	3.5	1.6	1.5	1.5	1.5
Screen Analysis		% Retained			
Tyler Mesh					
3	0.0	0.0	0.0	0.0	0.0
10	1.7	0.0	37.2	6.8	0.0
20	10.9	12.8	22.1	31.3	8.1
35	26.3	29.6	16.9	25.2	29.7
48	17.8	20.0	--	--	--
60	--	--	8.9	13.1	21.2
100	14.9	14.1	5.3	8.3	14.2
200	14.4	12.0	4.4	7.1	11.4
PAN	19.0	11.5	5.2	8.1	15.4
	100.0	100.0	100.0	100.0	100.0

The specific lances used were pitch impregnated graphite and were composed of essentially 99 percent carbon and a typical 0.13 percent ash (the pitch impregnation material being graphitized out during either processing by the manufacturer or preheating in the experimental combustor). The lances were obtained in either six or eight foot lengths with a three inch O.D. and a 3/4 inch I.D. Refractory material used to line the induction furnace during experimentation included high alumina dry ram material (Inducto - 87A), high alumina castable material (Harmix CU) and a high alumina brick (Korundal XD). The specific properties and compositions of these refractories are shown respectively in Tables III-A, IV-A, and V-A.

TABLE III-A

INDUCTO - 87A REFRACTORY

Technical Data:

Maximum Temperature	-	3500°F
Density	-	195 lb/ft^3
Chemical Nature	-	Amphoeteric
Thermal Conductivity	-	26 btu/in @2500°F
Mean Specific Heat	-	.22 btu/lb/ft
Modulus of Rupture (After Firing)	-	700 lbs/in^2 @2500°F
Thermal Expansion	-	.05% @2000°F

Chemical Analysis:

Alumina (Al_2O_3)	-	90.5%
Silica (SiO_2)	-	6.6%
Magnesia (MgO)	-	trace
Zirconium Oxide (Zr_2O)	-	trace
Calcium Oxide (CaO)	-	trace
Iron Oxide (Fe_2O_3)	-	trace

Experimental Procedure

The experimental program consisted of three types of specialized operations: carburization tests, decarburization tests, and slag injection. All these experimental operations began with the basic combustor startup; the individual differences beginning at certain points per the following discussions.

The combustor startup procedure began with a detailed clean-out of the induction furnace interior to remove all foreign material. A specified amount of iron was then charged into the furnace in starter

TABLE IV-A

HARMIX CU REFRACTORY

Technical Data:

*Physical Properties: (Typical)

Weight Required for Ramming	
If Shipped Dry	173 pcf
If Shipped Wet	180 pcf
Approximate Amount of Water Required for Ramming Dry Mix	
Per 100 lbs.	2 U.S.Qts.
Per 45.36 Kg.	
Bulk Density	lbs./cu.ft.
After Drying at 230°F. (110°C)	173
Modulus of Rupture	lbs./sq.in.
After Drying at 230°F. (110°C)	400 to 800
After Heating at 2300°F. (1260°C)	1500 to 2500
Cold Crushing Strength	
After Drying at 230°E (110°C)	2500 to 4500
After Heating at 2300°F. (1260°C)	8000 to 10,000
Permanent Linear Change (%)	
After Drying at 230°F. (110°C)	Negligible
After Heating at 2300°F. (1260°C)	0.0 to +0.5

*Chemical Analysis:	Silica	(SiO_2)	11.4%
(Approximate)	Alumina	(Al_2O_3)	84.6
(Calcined Basis)	Titania	(TiO_2)	2.8
	Iron Oxide	(Fe_2O_3)	1.1
	Lime	(CaO)	Trace
	Magnesia	(MgO)	Trace
	Alkalies	($Na_2O+K_2O+Li_2O$)	0.1

TABLE V-A

KORUNDAL XD REFRACTORY

Classification:	High Alumina Brick	
Physical Data: (Typical)	Bulk Density	
	Pounds/cu.ft.	181 to 185
	Grams/cc	2.90 to 2.96
	Apparent Porosity, %	14 to 18
	Cold Crushing Strength on Flat	
	Pounds/sq.in.	9000 to 14000
	Kilograms/cm^2	634 to 986
	Modulus of Rupture	
	Pounds/sq.in.	2500 to 3500
	Kilograms/cm^2	176 to 246
	Reheat Test	
	Permanent Change @	
	At 3140°(1725°C)	+0.5 to +1.5
	At 3300°F (1816°C)	+1.2 to +2.4
	Load Test, 1½ hr., 25 psi (1.76 kg/cm^2)	
	% Linear Change	
	At 3000°F. (1650°C)	0.0 to +0.4
	At 3200°F. (1760°C)	-0.2 to -0.4
	Load Test, 24 hr., 25 psi (1.76 kg/cm^2)	
	At 3200°F. (1760°C)	-1 to -3
	Panel Spalling Test	
	% Loss	
	Preheat - 3000°F. (1650°C)	0.0

Chemical Analysis: (Approximate)	Silica	(SiO_2)	8.5%
	Alumina	(Al_2O_3)	90.8
	Titania	(TiO_2)	0.1
	Iron Oxide	(Fe_2O_3)	0.2
	Lime	(CaO)	0.07
	Magnesia	(MgO)	0.07
	Alkalies	($Na_2O+K_2O+Li_2O$)	0.15

block and pig form. The transition base was then sealed, as air tight as possible, to the induction furnace using a non-binding asbestos refractory mud; the transition stack was then connected to the flare section. The induction furnace control panel and all auxiliary equipment were then inspected and started up proceeding to a molten iron bath. In the interim between furnace startup and the appearance of a molten iron bath, the sampling system analytical equipment was calibrated. Once a molten bath was established, the entire experimental combustor system was checked and started in sequence, beginning with the water flows, through the safety flare burner, and ending with the I.D. fan. Once the entire experimental combustor was operable, the desired tests were performed.

Decarburization testing began by preheating a lance sized to effect air injection at a specified depth. During the final minutes of the preheat cycle, the flexible air transport line from the trailer was connected to the lance and the air flow rate preset on a rotameter. Immediately prior to decarburization, iron and slag samples were taken. The lance was then lowered to the specified depth with air flow to prevent lance pluggage. The experiment was then carried out as prescribed. At the end of the test, the lance was withdrawn, weighed, and measured, while iron and slag samples were taken.

Carburization testing began with the charging of coal into the pneumatic injection system. During the lance preheat cycle mentioned above, the injection tank was pressurized to the specified amount using either nitrogen or air. Similar to decarburization testing, the flexible transport line from the injection tank was connected to the graphite lance during the final minutes of the preheat cycle. Experimentation began by lowering the lance into the iron at the end of the preheat cycle. As with decarburization testing above, iron and slag samples were taken before and after experimentation.

Slag synthesis was performed in the same manner as for the carburization. Prior to charging the slag ingredients into the injection tank, they were individually weighed and thoroughly mixed. Following mixing, the mixture was sampled and charged into the injection tank. As in the carburization test procedure, the ingredient mixture was injected beneath the molten bath. The materials then dissolved and floated to the top.

Gaseous Sampling and Analysis

During experimentation, samples of gas streams throughout the system were taken from gas sample taps and sampling ports located in the transition section, flare, and stack sections. The combustor offgas was continuously monitored by the various instruments located on the panel shown schematically in Figure A-4. The instruments determined the concentrations of oxygen, carbon monoxide, carbon dioxide, hydrogen, sulfur dioxide, nitric oxide, and nitrogen dioxide in the gaseous stream. Located on a separate panel were seven strip chart recorders

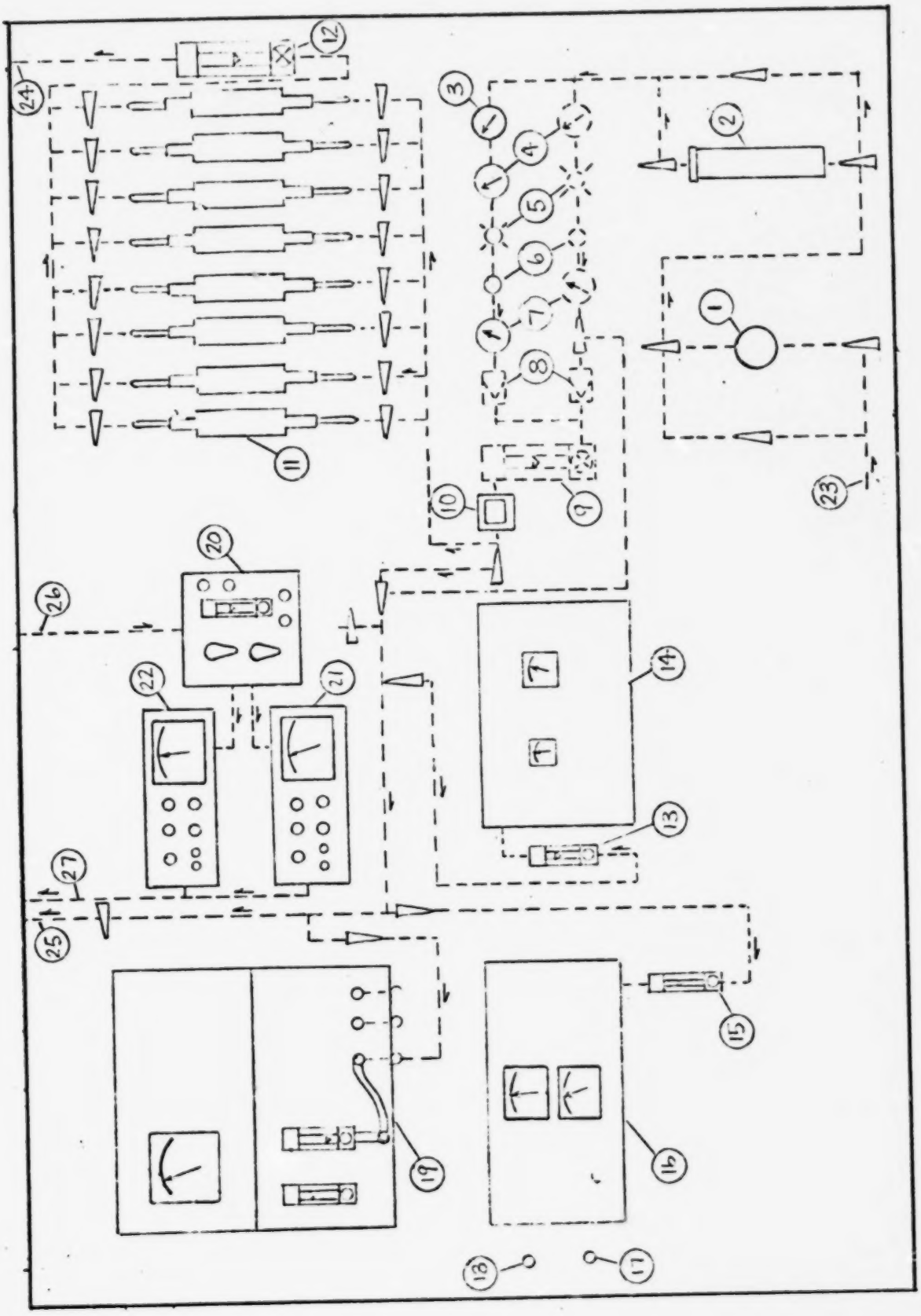

FIGURE A-4
ANALYTICAL INSTRUMENT PANEL SCHEMATIC

FIGURE A-4 (Cont'd)

ANALYTICAL INSTRUMENT PANEL DESCRIPTION

Item No.		
1.	Filter	0.3 microns
2.	Drierite	10-20 mesh
3.	Temperature Gauge	50-500°F
4.	Vacuum Gauge	0-30 in. Hg
5.	Main Pump Switch and "ON" Light	
6.	Relief Valve	
7.	Pressure Gauge	0-30 psi
8.	Check Valve	
9.	Main Flowmeter	0-50 SCFM
10.	Main Total Indicating Flow	
11.	Sample Bomb	
12.	Sample Bomb Flowmeter	0-50 SCFM
13.	Hydrogen Flowmeter	20-280 cc/min
14.	Hydrogen Analyzer	0-25%
15.	Carbon Monoxide and Carbon Dioxide Flowmeter	20-280 cc/min
16.	Carbon Monoxide and Carbon Dioxide Analyzer	0-50%
17.	Carbon Monoxide Trim Pot	
18.	Carbon Dioxide Trim Pot	
19.	Oxygen Analyzer	
20.	NO, NO_2 and SO_2 Control Module	0-5 SCFM
21.	Nitric Oxide Analyzer	0-500 PPM
22.	Nitrogen Dioxide and Sulfur Dioxide Analyzer	0-500 PPM
23.	Main Sample Inlet	
24.	Sample Bomb Outlet	
25.	Main Sample Outlet	
26.	Control Module Inlet	
27.	Control Module Outlet	

integrated with the instruments which provided a continuous record of these concentrations. The panel was also designed so that the sample gas stream could be split. Part of the gas was routed to the continuous analyzers and another part of it was sent to a series of glass sample bombs which could be opened and closed to take retainer gas samples at various times during an experiment.

Analytical System Operation

Flow meters are located on the panel so that flows can be independently adjusted to the instruments. A stainless steel bellows pump is used to pull the gas from the combustor and to deliver it to the instruments and glass sample bombs. This type of pump was chosen since no lubricating oils or foreign material contacts the sample gas except the AM-350 stainless steel bellows which are inert to reaction with combustor gases. Also located on the panel upstream of the pump is a filter and a drierite column to remove water vapor from the stream. Pressure gauges, vacuum gauges, and thermometers are also mounted on the panel to monitor the sample gas characteristics.

Gas sampling ports are located at several positions in the area of the transition section of the combustor. Sample taps at this section are prone to plugging; therefore, a manifold arrangement is provided so that switching from one sample port to another can be done quickly during the course of an experiment if desired. The sample line itself is 1/4 inch stainless steel tubing and runs from the combustor sample ports into an adjacent room in which the instrument panel is located. The approximate hold up time in the line is 15-30 seconds. The response time of the instruments ranges from less than one second to about ten seconds. A brief description of each of the continuous gas analyzers is given below.

SO_2, NO_2, NO_x Analyzers

The instruments for monitoring sulfur dioxide, nitric oxide, and nitrogen dioxide in the combustor offgas were manufactured by Envirometrics, Inc., (Marina Del Rey, California). The measurement of these gases is accomplished by using patented plug-in sensors which Envirometrics calls Faristors™. According to Envirometrics, the Faristor is a liquid-state device containing a chemically-sensitive activating surface layer upon which pollutant molecules are strongly adsorbed by non-thermal catalytic action. This results in a change of oxidation state producing a charged surface relative to a reference layer. The magnitude of this charge is determined by the rate at which the gas molecules reach the activating surface, this in turn being directly proportional to the pollutant concentration at a constant sampling rate. Transfer of this charge across the activating layer results in a current flow. The net effect is somewhat analogous to a negative (nonohmic) resistance in a solid-state device. Faristors are made individually selective by virtue of the specific free energies of reaction and varying chemical kinetics associated with the catalysis of the individual pollutants*. The equipment includes three separate instruments (shown as item numbers 20, 21, 22, on Figure A-4). Item number 20 is a sampler control module which contains a stainless steel bellows pump, water trap, and

*"Instruction Manual, Coupled SO_2/Nitrogen Oxide Analyzers", from Envirometrics, Inc.

and dust filter. This module conditions the gas sample before it is sent to the NS-280 analyzer. The NS-280 analyzer contains Faristors to measure SO_2 and NO_2 concentrations (2-10,000 ppm). The sample gas then passes into the NS-200 analyzer which determines NO (2-10,000 ppm). The NS-200 and NS-280 analyzers are equipped with analog output signals (0-10 mv) which are connected to strip chart recorders.

Calibration gases are located behind the instrument panel and are connected directly to the sampler control module. By adjusting the three way ball valves on the module, the calibration gases can be sent to the analyzers. The following calibration gases are required: nitrogen, nitric oxide in nitrogen, nitrogen dioxide in nitrogen, and sulfur dioxide in nitrogen. A complete calibration is performed weekly but zero and span checks are done approximately every hour (while the instruments are in service).

Hydrogen Analyzer

A Bendix Thermal Conductivity Monitor is employed to determine the amount of hydrogen present in the sample gas stream. The principle of thermal conductivity is used in many continuous analyzers. The value of the thermal conductivity of a gas is indicative of its ability to remove heat from its surroundings. Hydrogen has a very high thermal conductivity and can remove heat rapidly compared to gases such as nitrogen and oxygen which have lower themal conductivities and remove heat slowly. The thermal conductivity detector has a sealed reference cell filled with air and a measuring cell through which the sample gas passes. The detector elements are WX, 32 ohm filaments which are part of a Wheatstone bridge, which in turn heats the filaments. As hydrogen passes through the measuring cell, heat is conducted from the filament, changing the resistance and changing the current flow in the bridge. The change in current is proportional to the concentration of hydrogen.

The instrument has a range of 0-25 percent hydrogen. Calibration is done on a daily basis (when operating) and includes the use of a zero gas (air or nitrogen) and a span gas (a gas mixture containing 18 percent H_2, 28 percent N_2, 54 percent CO).

CO, CO_2 Analyzer

Analysis of the sample gas stream for carbon monoxide and carbon dioxide is accomplished with a Peerless #206 two-gas analyzer manufactured by the Peerless Instrument Company, (Elmhurst, New York.) The operation of the instrument is based on the selective absorption of radiation of certain wave lengths by CO and CO_2. According to Peerless, "The infrared (IR) radiant energy from the sources is formed into two beams: the reference beam and the sample beam. The gas in the sample cell absorbs IR in proportion to the gas concentrations while the reference cell contains a neutral gas... The difference in energy in the two beams coming out of the two cells (and ultimately reaching detectors)

is proportional to the gas concentrations in the sample"**. The signal beams striking the detectors are ultimately transformed into electrical signals which are noted on two meters located on the front of the instrument. The electrical signals are also sent to strip chart recorders for the two gases.

The range of the instrument is 0-50 percent for both carbon monoxide and carbon dioxide. Zero calibration is done with air or nitrogen while the span calibration is done by either using a gas mixture containing CO and CO_2 or by using the convenient "internal" calibration knob located on the front of the instrument. Calibration is done on a daily basis while operating.

Oxygen Analyzer

The oxygen analyzer used was manufactured by Servomex Controls and was distributed by Bendix. The operation of the instrument is based on the fact that oxygen exhibits paramagnetism to a much greater extent than other common gases. Thus, the instrument is made to respond to the magnetic susceptibility of the sample being tested. This response is eventually transformed into a meter reading denoting the percent oxygen in the sample directly. This is accomplished according to the following description given by Bendix: "Inside the instrument, a small dumb-bell shaped body is suspended on a platinum ribbon in a non-uniform magnetic field. It experiences a torque which is proportional to the volume of magnetic susceptibility of the gas surrounding the dumb-bell. This torque is counteracted by the electro magnetic effect of current which is made to flow through a single turn of platinum wire wound around the dumb-bell. The current required to do this is proportional to the original torque and is, therefore, a measure of the susceptibility of the sample gas."

The range of the instrument is 0-25 percent oxygen. Calibration is done on a daily basis using two calibration gases: (1) nitrogen to obtain a zero check, and (2) air to obtain a span adjustment (21 percent oxygen).

Iron and Slag Sampling Analysis

Iron samples are obtained with "batester" immersion sampling devices. The devices operate on a simple capture and freeze principle in that when the end reaches molten metal, a protective cap melts and allows metal to enter a sample chamber where it solidifies into a pin sample with an enlarged retainer sample at one end.

Slag samples are obtained using a rod with a cupped end. Representative samples are taken by immersing the rod to a specified depth at a given location in the fluid slag. Both the iron and slag samples are taken through sample ports located on the transition section and are analyzed primarily for carbon and sulfur.

**"Operation and Service Manual", Peerless Instrument Co., Inc.

The procedure used to determine the amount of carbon that is contained in the above iron samples taken from the molten bath is based on the combustion method of carbon analysis. In this method, the carbon contained in the sample is burned to carbon dioxide; the amount of carbon dioxide produced is measured and the percent carbon in the sample is subsequently determined.

The experimental equipment is shown in Figure A-5. The oxygen used for combustion is treated in a Leco purifying train (#516-000) prior to entering the furnace in which the combustion occurs. The purpose of the purifying train is to remove trace amounts of moisture, carbon dioxide, and acid gases that may be present in the oxygen. These gases, if not removed, would interfere in the present method. The furnace in which the combustion takes place is a Burrell Model H-9 resistance furnace. The furnace is heated by four symmetrically arranged glow bars which surround and are parallel to the ceramic reaction tube. The temperature is controlled by two voltage taps located on the front of the furnace. The exit end of the combustion tube is packed with glass wool to trap dust particles produced during combustion. The gas leaving the furnace then passes through a MnO_2 trap to remove sulfur oxides and then to the Leco gasometric carbon analyzer (#572-100). The Leco carbon analyzer traps all of the gases that exit the furnace (except sulfur oxides) during the entire combustion procedure. These gases consist primarily of oxygen and carbon dioxide. The volume of this gas at standard conditions is measured on a graduated burette located below the large bulb on the analyzer. The gas is then contacted with a concentrated solution of caustic (KOH) to remove the carbon dioxide. After removal of CO_2, the gas is sent back to the bulb outfitted with the graduated burette. The difference in volume represents the amount of CO_2 that was originally present in the offgas. The amount of carbon present in the sample is, of course, directly proportional to the volume of CO_2 produced.

The experimental procedure consists of (1) sample preparation, (2) combustion of the sample at 2400-2700°F with an oxygen flow rate of 1 liter/minute, (3) measurement of the offgas produced, (4) scrubbing the CO_2 from the offgas, and (5) measuring the volume of offgas less carbon dioxide. Sample preparation consists of crushing the disc-pin iron sample in a mortar and pestle into small fragments. Approximately 200 milligrams of sample is placed in a ceramic combustion boat. The following combustion accelerators are added: one scoop (1 gram) of copper coated tin and two strips of copper. The combustion boat containing the sample is then placed into the furnace for one to two minutes to preheat, followed by introduction of an oxygen flow rate of one liter per minute. After a ten minute burn time, the products of combustion are scrubbed with the caustic solution and the volume is then remeasured to find the volume of carbon dioxide produced in the combustion. The percent carbon in the iron sample is then calculated from the amount of carbon dioxide produced.

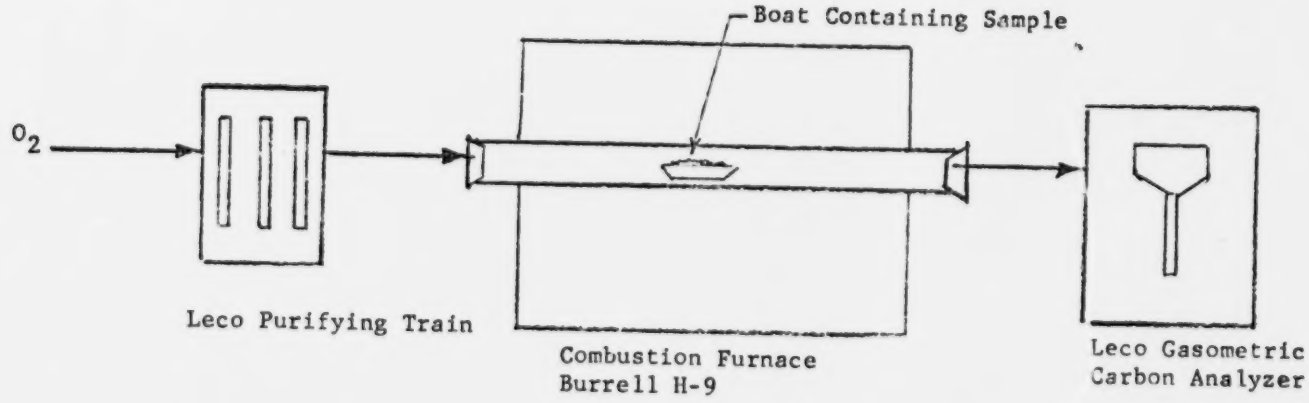

FIGURE A-5

CARBON DETERMINATION EQUIPMENT

The determination of the percent sulfur contained in iron and slag samples is based on the combustion-iodometric method. In this method, the sulfur in the sample is burned to sulfur dioxide which is subsequently titrated with potassium iodate to determine the amount of SO_2 that evolves from the sample. The reactions proceed according to the following equations:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O \quad (1)$$

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI \quad (2)$$

Thus, the SO_2 that is formed during combustion is bubbled into a titration vessel containing a weak solution of HCl to which has been added potassium iodide and starch. The titrant is KIO_3. Equation (1) above produces free iodine which forms a deep blue complex with starch. As sulfur dioxide enters the solution, it is rapidly oxidized to sulfuric acid. This oxidation reaction also destroys the free iodine and, therefore, the blue color caused by the starch-iodine complex. Addition of KIO_3 titrant restores the blue color until additional SO_2 evolves from the combustion of the sample. Persistance of a blue color in the titration vessel indicates the absence of sulfur dioxide. The total amount of sulfur dioxide that evolves during the combustion is determined by the amount of KIO_3 titrant added (three moles of SO_2 are equivalent to one mole of KIO_3).[3]

The experimental equipment is essentially the same as shown in Figure A-5, (determination of carbon in iron). In place of the Leco carbon analyzer is a Leco sulfur titrator model (#517). This titrator operates on the combustion-iodometric method described above.

Sample preparation for determination of sulfur in iron consists of crushing the sample and placing 100-200 milligrams in a combustion boat with 1 gram of copper coated tin and two strips of copper combustion accelerators. The combustion boat is then placed in the furnace at 2200°F and allowed to preheat for two minutes prior to initiating the flow of oxygen at one liter per minute. The boat is placed inside a thimble located in the hot zone of the furnace as shown in Figure A-6. The purpose of the thimble is to lower the rate at which the SO_2 would enter the titration solution. Without such an arrangement, SO_2 would evolve too rapidly and would escape before the titration procedure could be conducted properly. This arrangement is used for determining sulfur in both iron and slag samples and permits the entire titration to be extended to ten minutes.

The determination of sulfur in slag is done similarly except that, sample preparation consists of crushing the slag samples and removing foreign iron particles by magnetic separation before the sample is placed in a combustion boat with 1/2 gram of electrolytic iron accelerator, 1/2 gram of copper tin accelerator, and 2 strips of copper accelerator.

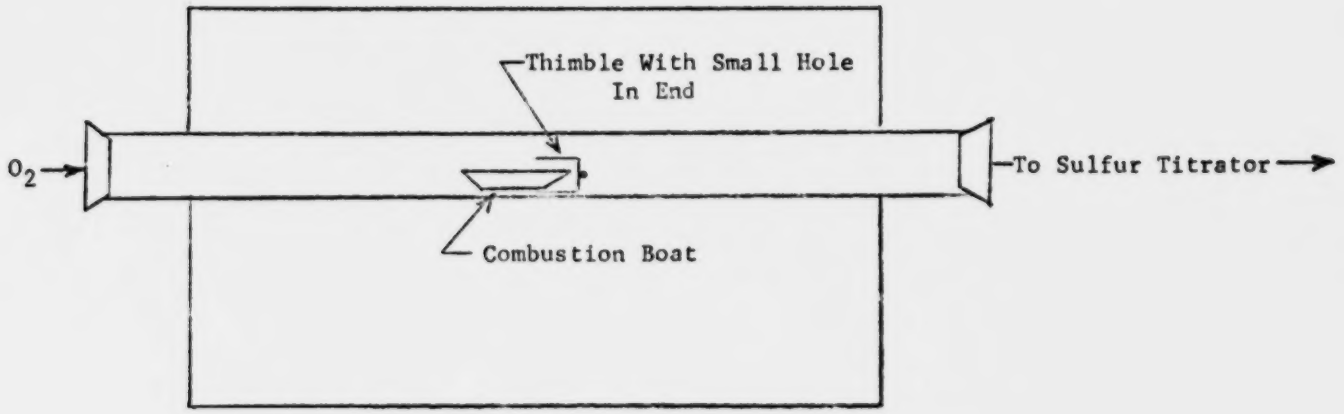

FIGURE A-6

SULFUR DETERMINATION EQUIPMENT

The chemical analyses for SiO_2, Al_2O_3, Fe_2O_3, and CaO in combustor slag samples utilizes both volumetric and gravimetric methods.

The first part of the analysis is a gravimetric analysis to determine SiO_2. The crushed slag sample is placed in a one to one solution of HCl and H_2O. The solution is filtered with coarse filter paper. The material remaining on the filter paper consists chiefly of SiO_2 and other acid insolubles. The filter paper and its contents are placed in a platinum crucible and fused with sodium carbonate to form soluble carbonates from the acid insoluble constituents in the slag. The fused material is then redissolved in concentrated HCl. Fifty milliliters of water are added and the solution is brought to a gentle boil. This solution is then filtered again to remove insoluble SiO_2. The filter paper is placed in a platinum crucible and charred at 200°C in a muffle furnace. After the paper has been charred off, the crucible is placed in a muffle furnace at 1000°C for several hours until a constant weight is achieved. The contents in the crucible are then reacted with 5-10 cc of concentrated hydroflouric acid. Silica in the crucible forms gaseous SiF_4 and escapes. After the excess HF has been driven off, the crucible is reweighed. The difference in weight represents the loss of silica as SiF_4. From this weight loss and the original sample weight, the percent SiO_2 in the sample can be determined.

The filtrate from the above filtration contains soluble forms of the calcium oxide, iron oxides, and alumina originally present in the slag. Ammonium hydroxide is added to the filtrate and the hydroxides or iron and alumina are precipitated. The precipitate is then filtered from the solution, washed, dried, and weighed. The weight recorded is proportional to the total weight of iron and aluminum in the original sample existing as Fe_2O_3 and Al_2O_3 (denoted as R_2O_3).

The filtrate from the above precipitation is retained to determine the amount of calcium in solution, and therefore, the amount of CaO existing in the original sample. Calcium is determined by performing a complexiometric titration with EDTA. This is a well known titration and is routinely performed. The filtrate is diluted to volume in a volumetric flask and an aliquot is extracted. The aliquot is buffered, calcine indicator is added, and the titration with EDTA is performed. The end point is achieved when the green flourescence seen in UV light and caused by a free calcium-calcine indicator complex dissappears.

The determination of the relative amounts of Al_2O_3 and Fe_2O_3 present in the sample from the total amount of these components (R_2O_3) is accomplished by analyzing for Fe_2O_3. A new slag sample is taken and digested in a 50 percent HCl solution. The iron is then reduced to the ferrous state with stannous chloride ($SnCl_2$) and titrated with a standard solution of potassium dichromate ($K_2Cr_2O_7$). This is known as the ferric oxide referee method (ASTM #C114).

APPENDIX B

LABORATORY STUDIES

Summary of Laboratory Results

To provide guidelines for conducting the experimental combustor program, a laboratory program was completed to ascertain the physico-chemical characterization of slags. In addition to the operational guidelines, engineering data were also generated for the process engineering studies. The results of the laboratory work can be summarized as follows.

Slag Composition

Slags having good fluidity or flow characteristics and partition ratios in excess of 20 can be produced with basicities of 0.2 or less. A 0.2 basicity slag composed of 20 percent CaS, 13.4 percent CaO, 44.4 percent SiO_2, and 22.2 percent Al_2O_3 is suitable for combustor operation.

All percentages are given on a weight basis. The use of higher basicity slags will result in poorer flow characteristics. No attempt was made to study additional effects of iron oxide on flow characteristics. However, it can be safely surmised that improved fluidity will be observed under actual conditions due to the inclusion of iron oxides and alkaline constituents into the slag.

Slag Viscosity

For slags having the composition specified above, the apparent viscosity over the temperature range of 2700 - 2800°F will be 50 to 100 poise. These data were obtained with an oscillating bob viscosimeter which tends to report higher viscosity values if the slags contained suspended solids. Inasmuch as the high sulfur bearing slags contain undissolved CaS, the measured viscosity is believed to be substantially higher than anticipated in the combustor.

Equilibrium Partition Ratios

For typical lime-silica-alumina slags covering a basicity range of 0.2 to 1.0, equilibrium sulfur partition ratios in excess of 20 will be realized. These values were for a slag containing 20 percent calcium sulfide (approximately 8.9 percent sulfur).

Heat Capacity

For slags containing 20 percent calcium sulfide, the heat capacity shows no dependence on slag basicity. Consequently, for process engineering calculations, the heat capacity of 20 percent CaS bearing slags is adequately defined by

$$C_p = 0.119 + 3.66\times10^{-4}T - 15.90\times10^{-8}T^2$$

which is valid over the temperature range of 200 to 1200°C. In the equation,

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specific heat has the units of calories per gram per degree C, and T is defined as degrees K.

Crushing Energy Requirements

For sizing the necessary crushing and grinding equipment, the slags can be assumed to have characteristics comparable to silica. Comparison of crushing energy requirements for slag and silica indicates that the same Rittinger's Number characterizes both materials. The fact that the slags behave as silica during crushing should facilitate the selection of commercial equipment.

Slag Granulation

Experimental results indicate that a vacuum shot tower granulation method is an effective means of increasing the total surface area of typical $CaO-SiO_2-Al_2O_3$ slags from two to five times the value for crushed slag. Based on these findings, it appears that slag granulation can serve as a means of providing increased total surface area slags for desulfurization.

Slag Desulfurization

Experimental results indicate that slag desulfurization is mass transfer controlled and no chemical reaction kinetics limitations are present. Although complete design information is not yet available, it is believed that reasonably sized reaction vessels can be used. Experimental results have shown that 99 plus percent desulfurization occurs with an offgas containing approximately 50 percent sulfur.

SLAG FLUIDITY

Introduction

The operating cost of the process is influenced to a large degree by slag fluidity and the ability of the slag to contain a maximum amount of sulfur. The slags must be fluid enough to facilitate removal from the combustor but at the same time they must be viscous enough to minimize refractory corrosion[3,4]. Consequently, a compromise slag fluidity is required to maintain the most desirable operating conditions. Ideally, the slag should satisfy not only the fluidity requirement but it should also contain the stoichiometric equivalent of lime to convert all of the sulfur introduced to the molten iron bath by the coal to calcium sulfide. However, from a practical viewpoint an excess of lime will be required.

Because the ATC process requires a low excess lime content in the slag, very low basicity (defined as the ratio of lime to the sum of the silica and alumina contents) high sulfur slags will be required. A great deal of data are available[5] pertaining to the effect of slag composition on the viscosity of slags containing less than 2 percent sulfur. However, combustor slags will contain about 6 - 8 percent sulfur. The only available data for such high-sulfur slags were obtained using high-basicity magnesia-bearing slags[2]. In power plant application of the ATC combustor, the use of magnesia-bearing high-basicity slags would have an adverse economic effect by increasing the quantities of flux added to the combustor. The choice of limestone and the

composition of the coal ash restricts the slag composition to the $CaO-SiO_2-Al_2O_3$ system. Most coals used for power generation contain an ash whose composition is relatively fixed at a silica to alumina ratio of about two[6]. Since the flux to be added to the combustor contains only minor amounts of silica and alumina, the slags produced will contain silica and alumina in the same proportion as that found in coal. For this reason this ratio was maintained in all experimental work. Since literature data on the effect of high sulfur concentration on slag viscosity are scarce and because a large number of slag compositions are possible, a quick screening test was required to relatively rank the various types of slags with regard to fluidity. A simple and rapid fluidity test has been developed by Herty [7,8] and has been used in steelmaking operations for some time.[9] The test with some modification has proven to be a valuable aid for the evaluation of slag fluidity characteristics.

The principle of the test is to cause molten slag to flow down an inclined plane. The extent to which the slag travels down the plane prior to solidification is an indication of its fluidity (and, indirectly, viscosity). Obviously, a test as simple as this is influenced by a number of physical constants as well as heat transfer. Nevertheless, it is used as a relative guide for comparing differences in fluidity[2] and was adopted for use in this work.

Experimental Procedure

Ten different compositions of slag (Table IB) with varying amounts of CaS and basicities ranging from 0.2 to 1.2 were used for this investigation. Five pounds of each of these slags were prepared from reagent grades of CaO, Al_2O_3, SiO_2, and CaS by melting at 2700°F with an argon atmosphere in a

TABLE I-B

Premelt Composition of Slags

Slag No.	Basicity	Weight Percent CaO	Al_2O_3	SiO_2	CaS
1	.80	40.4	16.9	33.7	9.0
2	.80	35.6	14.8	29.6	20.0
3	1.00	45.5	15.2	30.4	9.0
4	.50	26.0	18.0	36.0	20.0
5	1.00	39.9	13.3	26.6	20.0
6	1.20	49.6	13.8	27.6	9.0
7	.20	13.4	22.2	44.4	20.0
8	.80	38.0	16.0	31.0	15.0
9	1.00	51.5	16.5	32.0	0.0
10	1.00	42.5	14.2	28.3	15.0

covered pyrolitic carbon crucible. It required three soaking periods of eight hours each and periodic stirring to obtain slags of uniform composition. Uniformity of the slags was judged by their appearance. The slags were cooled, crushed and stored prior to conducting the Herty tests. Samples of approximately 300 grams each were remelted and used for the Herty tests. These tests were conducted at temperatures of 2600°F, 2650°F, and 2700°F.

A schematic arrangement of the modified Herty apparatus is shown in Figure 1B. The apparatus contains two concentric pyrolytic graphite cups each having a 0.5 inch diameter hole in its base. The cups rest in a refractory brick cavity designed to accommodate the crucibles. This assembly rests on a platform attached to the top of an inclined plane. The inclined plane, (6 x 30 inches) is positioned at an angle of 14 degrees from the horizontal. Although a 30-degree angle is recommended in the Herty[5] procedure, the 14-degree angle was adopted so that the slag would remain intact after solidification. It was found that an inclination of 30 degrees was too steep and as a result, the slag upon solidifying tended to break up and slide down the inclined plane.

In conducting the Herty tests, the two concentric cups (one placed inside the other, bottom holes 180° apart) and the graphite thermowell are heated to the respective slag temperatures. The holes in the cups are mis-aligned to prevent slag flow until the start of the test. These crucibles along with the refractory brick, (heated to 2000°F) are positioned on the platform at the top of the inclined plane. Molten slag is then poured into the inner cup. The holes of the cups are then aligned so that the molten slag will flow from the crucible and down the incline plane.

The temperature of the slag, the length and weight of the stringer are recorded.

Discussion of Results

Work completed for the Water Quality Office[2] has shown that the addition of calcium sulfide to slags containing magnesium oxide lowered the slag fluidity. The bulk of this work was conducted with slags having basicities of 0.8 or more. To determine if a similar effect could be observed for the magnesium-oxide free slags employed in this work, a series of fluidity tests were completed on slags over the basicity range of 0.8 to 1.2. The results of this work, in which the slag calcium sulfide content was varied from zero to 20 weight percent, are presented in Table IIB. The data indicate that slag fluidity rapidly decreases with increasing calcium sulfide content. At a calcium sulfide content of 20 percent (which corresponds to the expected sulfide level in the commercial combustor), the slag showed a no flow condition. In these tests, a stringer length of zero inches indicates an apparent viscosity in excess of several thousand poise. Visual observation of the slags during the course of experimentation indicated that the slags were not solid but rather were very viscous and froze before any appreciable stringer could be formed. As the calcium sulfide content was lowered to 15 percent or less,

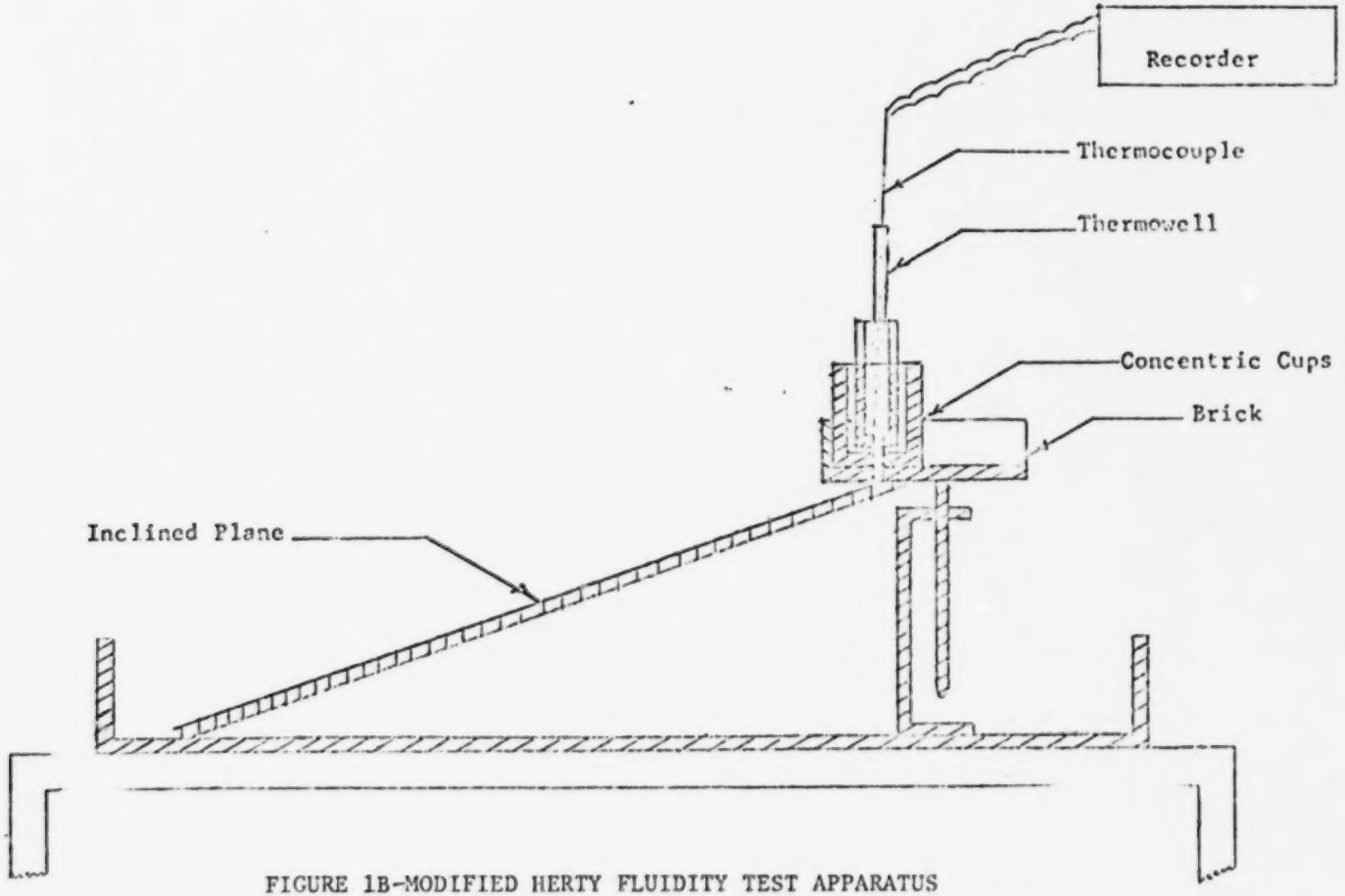


FIGURE 1B-MODIFIED HERTY FLUIDITY TEST APPARATUS

TABLE IIB

Effect of CaS Content on Fluidity of
High Basicity Slags

Slag Number*	Basicity	% CaS	Average Stringer Length Inches
6	1.2	20.0	0
9	1.0	0	31.0
3	1.0	9.0	24.3
10	1.0	15.0	0.0
5	1.0	20.0	0.0
3	0.8	9.0	11.0
8	0.8	15.0	3.0
2	0.8	20.0	0.0

*See Table IB for Compositions

acceptable flow characteristics were realized for the 0.8 basicity slags. The data suggest that increasing calcium sulfide content has a stronger effect on lowering the fluidity of the higher basicity slags particularly as the CaS content increases from 9 to 15 percent (compare 1.0 with 0.8 basicity slags).

The flow characteristics of multicomponent systems such as these slags are complicated functions of composition. Because such high basicities would require an excessive amount of flux (over and above that required to stoichiometrically combine with the sulfur) for the combustor, no further attempts were made to resolve the functional dependence of fluidity with varying calcium sulfide content. Instead, work was directed towards obtaining the fluidity or flow characteristics of economical slags containing 15 to 20 percent calcium sulfide. The results of this work are shown in Figure 2B. The data show that for slags containing 20 percent CaS (8.8 percent sulfur) decreasing the basicity increases the fluidity of the slag. As the basicity changed from 0.8 to 0.2 stringer length increased from zero to two inches. When the CaS content is decreased to 15 percent, the effect of decreasing basicity becomes more pronounced and even better fluidity characteristics are observed.

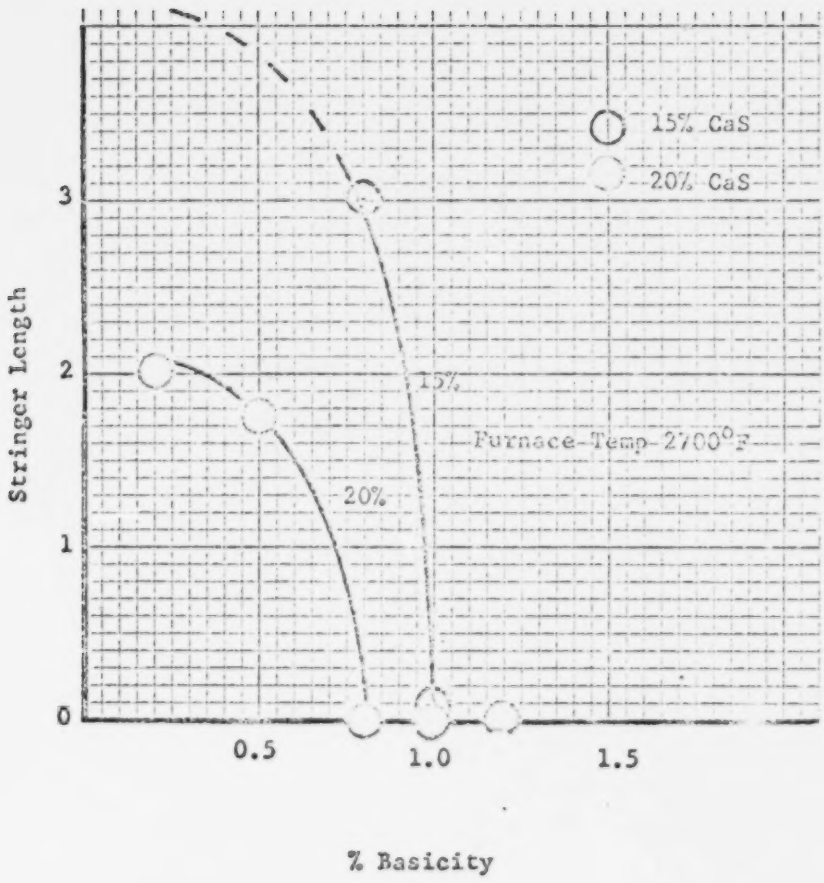


FIGURE 2B-EFFECT OF BASICITY AND CaS CONTENT ON SLAG FLUIDITY

Inasmuch as the fluidity measurement is only a relative guide and the data indicate that 0.2 basicity slags containing about 20 percent calcium sulfide can be poured and readily removed from the combustor, fluidity work was terminated in favor of more precise measurements of slag viscosity. As will be shown later, the choice of favorable slag compositions (about 0.2 basicity, 20 percent CaS) as determined by the Herty test is confirmed by the viscosimeter measurements.

SLAG VISCOSITY

Introduction

Fluidity test data discussed in the preceeding section establish the fact that the flow characteristics of the low basicity slags (0.2) are better than those obtained at higher basicity levels. It is important that the high-sulfur-bearing MgO-free slags have good flow characteristics so that they can readily be removed from the combustor. However, the slag must not be too fluid to prevent excessive erosion of combustor refractory. By maintaining a relatively low viscosity, using an MgO-free slag and producing a slag that contains about 10 percent sulfur, process economics and operability become attractive. Inasmuch as viscosity data are not available in the literature for the high-sulfur, MgO-free slags that will be used in the combustor, it became necessary to characterize the slags with respect to this property. For this reason, an oscillating bob viscosimeter with a high-temperature furnace capable of achieving temperatures of up to 3000°F was designed and constructed.

The theory and technique for determining viscosity with an oscillating bob will not be discussed in this report, as detailed explanations can be found in the literature [10, 11]. Briefly, the viscosity measurement is obtained by the logarithmic decrement of oscillation method. With this technique, an initial torque is applied to a torsion wire from which a serrated graphite bob is suspended and immersed in a molten slag contained in a graphite crucible. Depending on the magnitude of the viscous forces resisting the rotation of the bob, a characteristic dampened oscillation frequency occurs. The ratio of two successive dampened oscillation amplitudes is a function of the viscosity of the liquid.

Experimental Procedure

The viscosimeter illustrated in Figure 3-B was constructed by laboratory personnel and is similar to that employed by Machin et.al[11]. However, it differs from the equipment used by Machin in that the angular displacement of oscillation is measured by a gradual interruption of a beam of light focused on a photocell while Machin used a mirror that reflected light to measure the angular displacement. The output of the photocell is made proportional to the radial deflection of the suspended torsion wire. The photocell output is recorded with a Bausch & Lomb VOM 5 recorder. Except for this modification, and some changes with regard to the length of the torsion wires and a more convenient manner for setting the oscillating

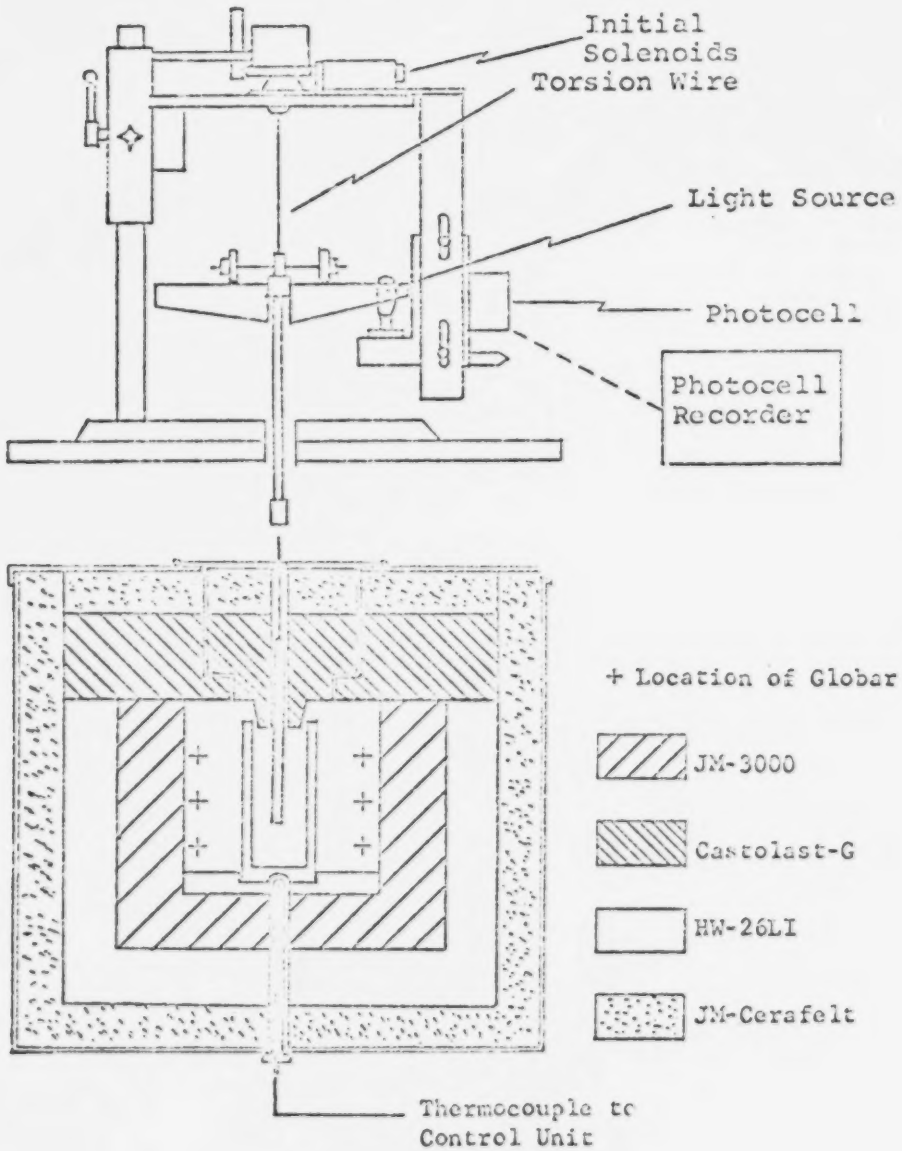


FIGURE 3-VISCOSIMETER AND HIGH TEMPERATURE FURNACE

system in motion, the two methods are the same.

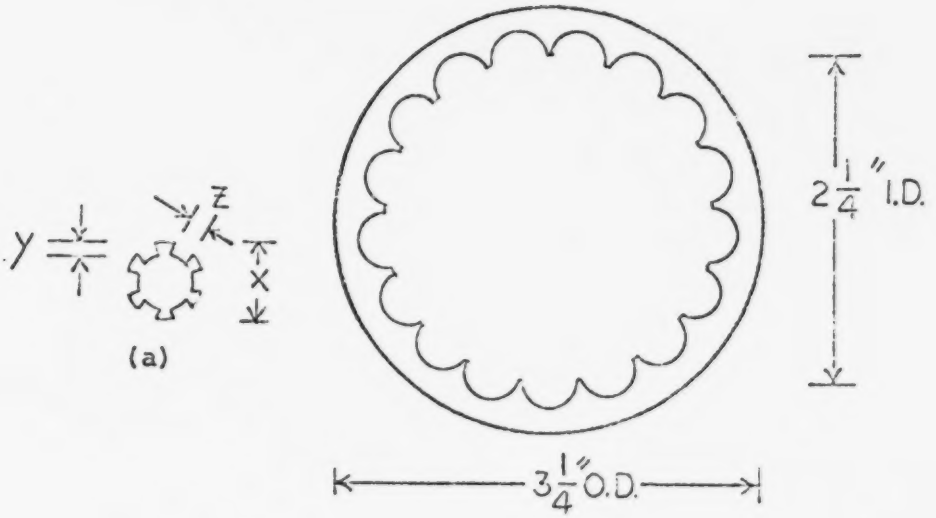
Graphite is used for both the oscillating bobs and the crucibles. Because the slags did not wet the graphite surfaces, both the bobs and the crucibles were grooved. The grooves were made parallel to the longitudinal axis of the bobs and crucibles (Figure 4-B). When the slag filled the grooves of both the bobs and the crucibles, a coating of molten slag adherred to the surface of the bobs and to the inside wall of crucible. This adherent coating is necessary for the measurement of viscosity, since the measurement depends on shearing stress between planes of different velocities. The rotation of the bob causes the slag to shear upon itself. The dampening constant is governed by the shape and dimension of the bob and crucible, the length and diameter of the torsion wire, the inertia of the mass suspended from the torsion wire, the immersion depth of the bob and, to a certain degree, the distance between the bob and the bottom of the crucible.

For the operating range of the viscosimeter, various pertinent factors and the calibration curves were determined with standard viscosity oils, the viscosities of which ranged from 3.9 to 620 poise at a room temperature of approximately 26°C. The equipment dampening constants were established for three certified torsion wire sizes (24, 27, and 30 B&S gauge) and two sizes of bobs.

The viscosimeter furnace is also shown in Figure 3-B. It has a cavity 9 inch deep by 8 inch wide by 8 inch high with an indentation located in the center of the bottom hearth plate for the graphite crucibles. The heating elements are located within this cavity. The cavity is accessible through a 5 inch diameter opening at the top. A gas inlet is provided at the bottom of the right side panel. The furance is capable of attaining the holding a temperature of 3000°F. The temperature is controlled with a Burrell Model SS-200 solid state controller, utilizing a Pt-13 percent Rh/Pt thermocouple, the tip of which is positioned flush with the bottom hearth plate.

To reduce atmospheric oxidation of the graphite bobs and the graphite crucibles at high temperature, the furnace was purged with argon for at least 1/2 hour prior to introduction of the crucibles containing the slag. Although the flow of argon was continued throughout most of the heating period, the entrance of air could not be prevented entirely. To prevent gas movement around the oscillating bob, the argon flow was discontinued during each viscosity measurement.

Attempts were made to check the validity of the equipment dampening constants under actual high temperature conditions with a standard lead-silica glass sample (NBS Sample No. 711). However, difficulties in sample



(a) Cross-sectional view of graphite bobs
large bob: x = 1/2" y = 1/16" z = 1/8"
small bob: x = 3/8" y = 1/16" z = 1/16"
length of bob = 12" Length of grooved section = 3"

(b) cross sectional view of graphite crucible
height of crucible = 7" inside
outside 7-3/4"

FIGURE 4-B-VISCOSIMETER BOB AND CUP

temperature measurement were encountered. The attempt was finally abandoned when it became apparent that PbO in the glass was reduced to elemental lead under test conditions. The validity of the equipment dampening constant under actual high temperature conditions was determined by using sulfur-free slags of known viscosities. These slags were prepared in the viscosimeter furnace with an argon atmosphere. During these experiments, the temperature of the slag at various depths was measured immediately after completion of the viscosity measurements. A two foot long Pt 13 percent Rh/Pt thermocouple was used for this purpose. The thermocouple was shielded by a two foot long quartz tube which was in turn protected from the slag by a thin graphite tip. It was noted that stray currents were interfering with the thermocouple and affecting the temperature measurements. Therefore, the power was turned off for short periods during each measurement in order to obtain reliable temperature readings.

Results and Discussion

Data obtained during instrument calibration with standard viscosity oil (Figure 5-B) showed that the distance between the bob and the crucible bottom has a small effect on the instrument dampening constant, which diminishes with increasing distance. This is reasonable because the presence of the crucible bottom is felt by the oscillating bob less and less as the distance between the bob and the crucible increases.

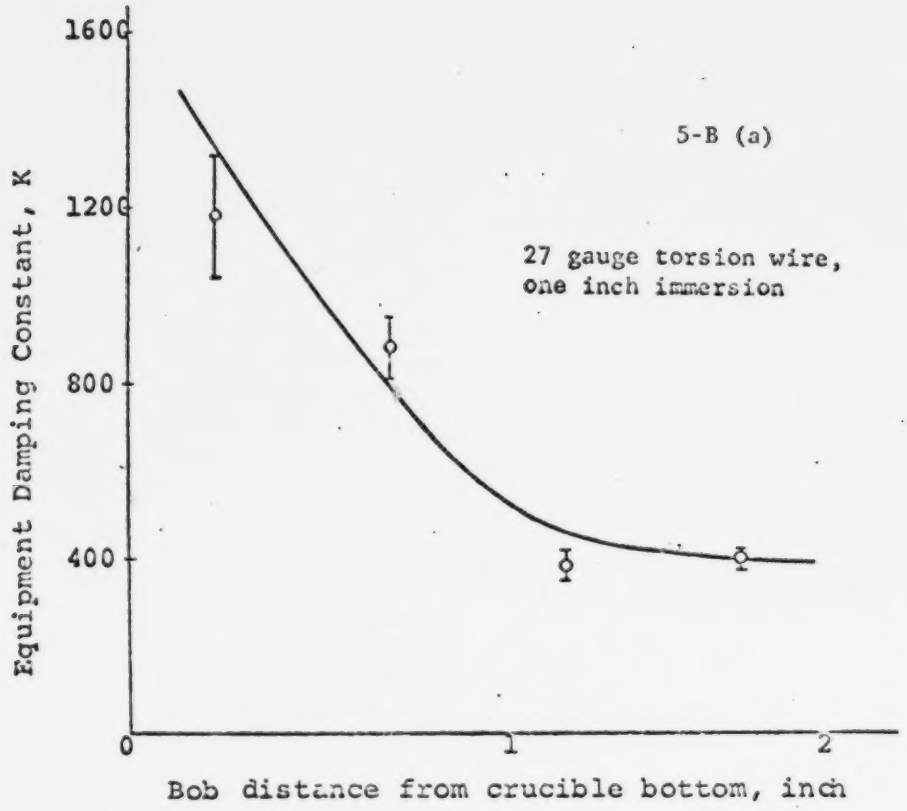
TABLE III-B

Effect of Immersion Depth on Equipment Dampening Constant (k) at Varying Bob Distance from Crucible Bottom

27 Gauge Torsion Wire and Small Bob Were Used

Bob Distance from Crucible Bottom	Average k value at immersion depth of:		
	3/4"	1"	1¼"
1"	684 ± 61	609 ± 91	797 ± 225
1¼"	648 ± 47	387 ± 33	878 ± 11
1½"	573 ± 73	479 ± 14	693 ± 17
1 3/4"	408 ± 35	404 ± 21	479 ± 43

Table III-B shows that at a bob immersion of 1 inch, the instrument dampening constant is least influenced by the bob distance from the crucible bottom for distances greater than 1 inch. Based on these calibration data, it was decided that an immersion depth of 1 inch and a distance of at least 1 1/4 inches from the crucible bottom should be used for all measurements except for slags of exceptionally high viscosities (1000 poise or more).



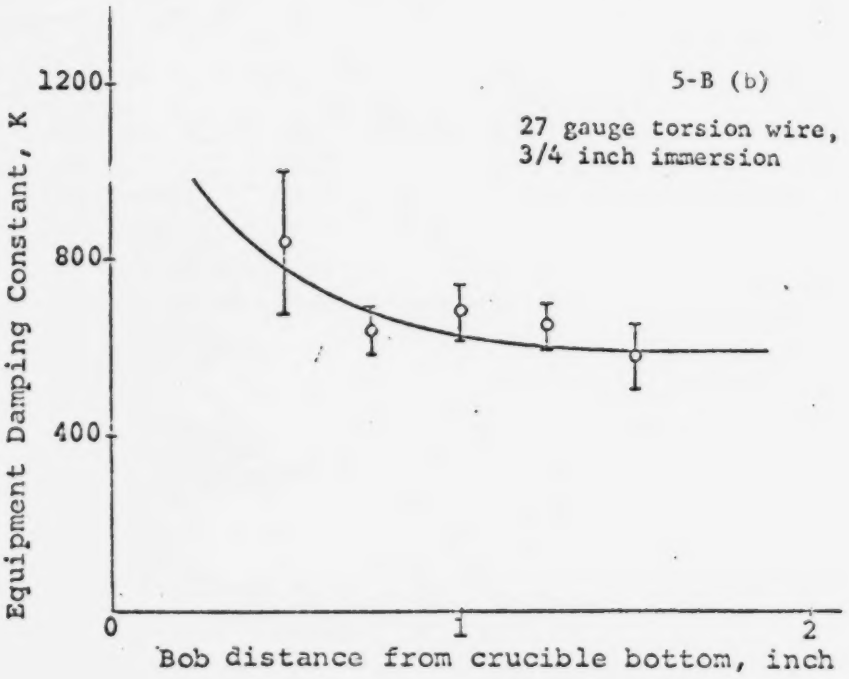


FIGURE 5-B-EFFECT OF BOB LOCATION ON DAMPENING CONSTANT

The k value (instrument dampening constant) that would be used in a particular measurement would depend upon the actual parameter governing that measurement, e.g. bob size, depth of immersion and the bob distance from the crucible bottom. To establish the validity of the instrument dampening constant obtained at room temperature with standard oils, a series of tests were completed at high temperatures using slags of known viscosities. Two slags for which literature values for viscosities were known were selected for these tests. The slag compositions are shown in Table IV-B for slags V-1 and V-2. The results of these measurements are shown in Table V-B which presents a comparison of the measure and literature[12, 13] values. In these experiments, the room temperature dampening constant was used to calculate the viscosity of the molten slag. As is evident, the observed viscosity agreed extremely well with the literature. For slag V-1 the reported reference [12] viscosity was 50 poise at a temperature of 2700 - 2732°F. The measured viscosity at 2680°F was 46 poise. However, since the literature only reported one point value, a second slag was tested for which the viscosity was known over a wide temperature range (Figure 6-B).

TABLE IVB

Premelt Slag Composition

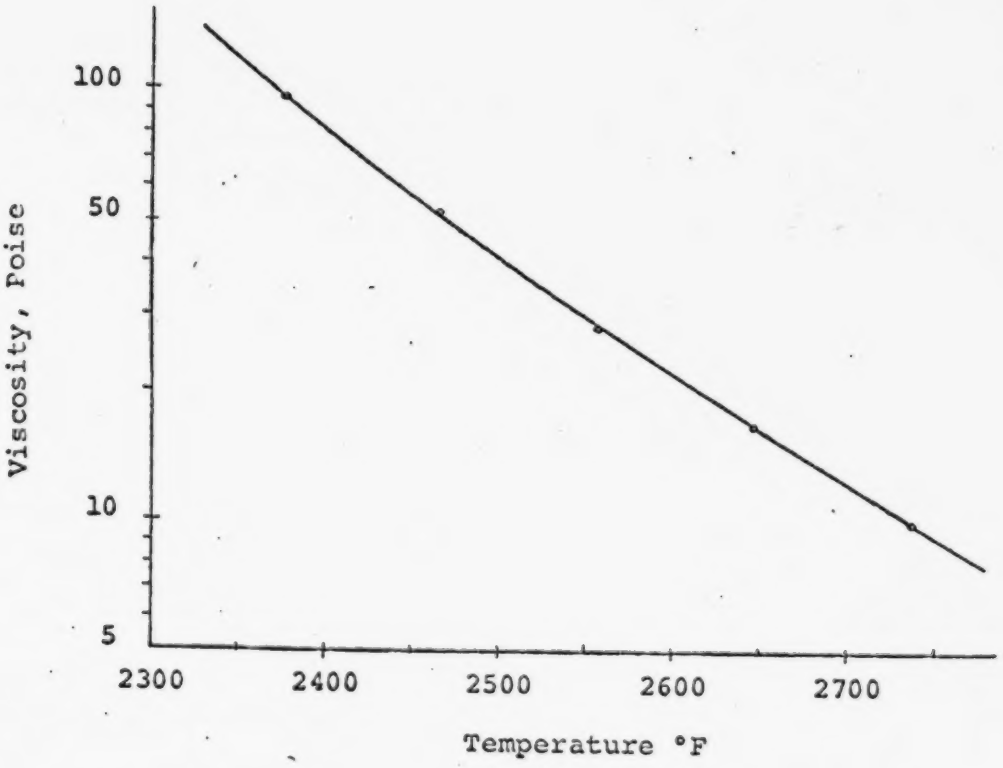
Slag No.	% CaO	$\%SiO_2$	$\%Al_2O_3$	%CaF	B/A Ratio
V-1	26	49.5	24.5	0	0.35
V-2	40	40	20	0	0.67

TABLE VB

Comparison of Measured Viscosity and Literature Values (12, 13)

Slag No.	Temperature °F	Observed, Poise	Lit., Poise	Reference
V-1	2680 ± 10	46 + 8	50 at 2732°F	12
V-2	2440 ± 10	58.4 ± 3.7	59 at 2440°F	13

For this slag (V-2) the observed viscosity at 2440°F was 58.4 plus or minus 3.7 poise which agrees extremely well with the literature [13] value of 59 poise. Based on these results, it was concluded that the effect of high temperature on the instrument dampening constant was small and that the room temperature calibration was equally valid at high temperatures.



Data Points Obtained from Reference No. 13

FIGURE 6-B-VISCOSITY OF SLAG V-2 (40% CaO, 40% SiO_2, 20% Al_2O_3)

Viscosity measurements were then made to determine the effects of temperature, slag sulfur content and slag basicity on slag viscosity. In Figure 7B is shown the effect of slag sulfur content on slag viscosity for 0.2 basicity slags. As seen, the slag viscosity increases with sulfur content. It is anticipated that slags with viscosities in the order of 50 poise or less will be sufficiently fluid for combustor operation; consequently, slag sulfur levels in the range of 6-8 percent are usable.

The effect of temperature and slag basicity on slag viscosity is shown in Figure 8B for slags containing 7.8 and 8.8 percent sulfur. As expected, slag viscosity decreases as the temperature increases. The viscosity also is seen to decrease as slag basicity decreases. For example, the slag viscosity is about 10 and 30 poise for basicities of 0.1 and 0.2 respectively at a temperature of 2750°F. Consequently, slags to be used in the combustor should have basicities in the range of 0.1 to 0.2.

It should be pointed out that the considerable scatter of the viscosity data obtained from the high sulfur bearing slag is attributed to the fact that at these sulfur contents, not all of the sulfur goes into the solution. The slags contain solid CaS particles that may be non-uniformly distributed within the slag mixture contained in the viscosimeter cup. Experimental result variability was artificially introduced into the measurement by swirling or mixing the slag prior to making a viscosity measurement. By swirling the slag, the solid CaS particles are forced to the outer perimeter of the cup and away from the oscillating bob. Consequently, the oscillating bob then measures the viscosity of slags containing little or no suspended solid particles. Because solid particles tend to yield higher apparent viscosities when measured with an oscillating bob viscosimeter, the stirred slag yielded lower viscosity values. Accordingly, it is expected that the apparent viscosities of high sulfur bearing slags measured in this equipment are probably substantially higher than the actual viscosities themselves. Visual observation of the molten slags as they are removed and poured from the viscosimeter indicate that the true viscosity will be considerably lower than the experimental values. These judgments are based on a relative comparison of the slag flow characteristics with those of the standard viscosity oils.

The above viscosity results were obtained for laboratory prepared synthetic slags. These slags did not contain FeO which will be present in actual combustor slags. The presence of even a small quantity of FeO has the effect of substnatially reducing slag viscosity[14]. Consequently, it is expected that in actual operation the slag viscosities will be much lower than the experimental results indicated.

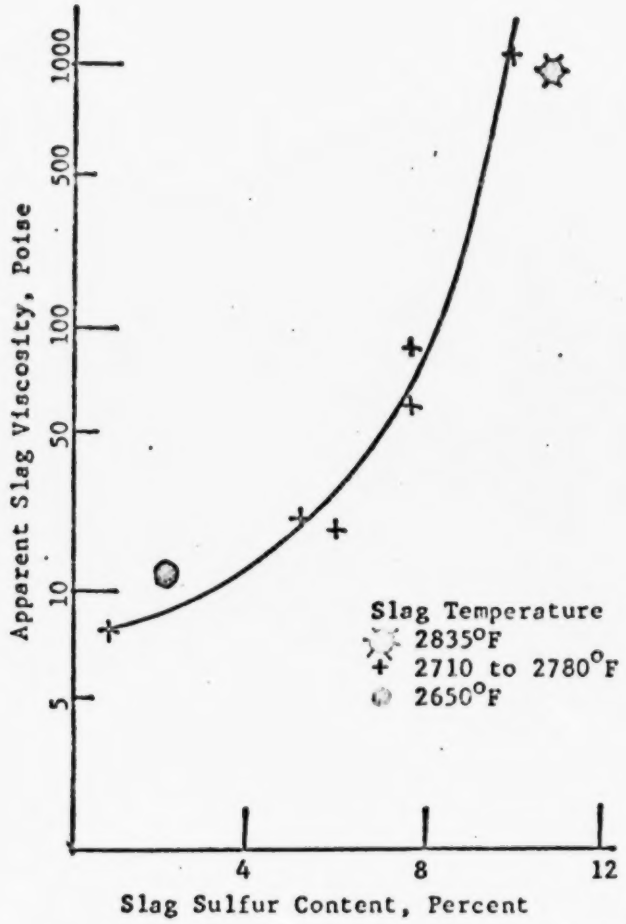


FIGURE 7B-EFFECT OF SULFUR CONTENT ON APPARENT VISCOSITY OF 0.2 BASICITY SLAG

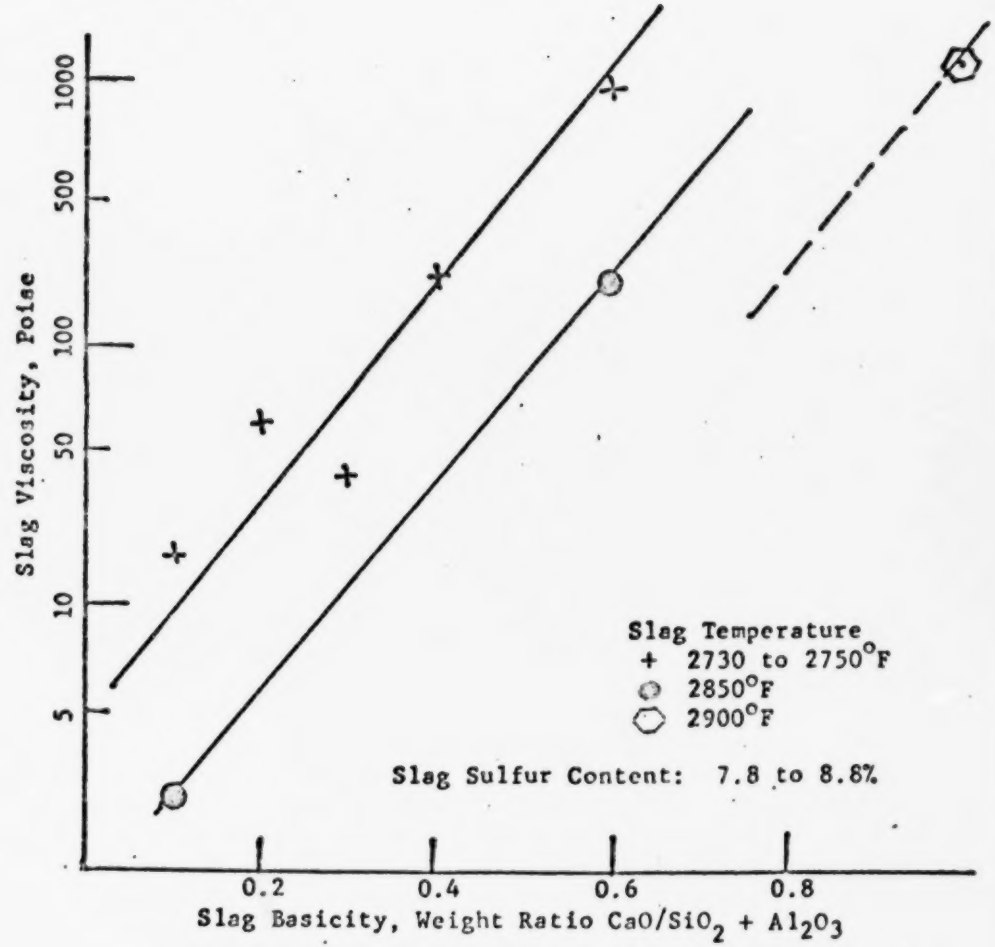


FIGURE 8B-EFFECT OF BASICITY ON APPARENT VISCOSITY OF HIGH SULFUR BEARING SLAGS

Based on the viscosity results of this section it can be concluded that low basicity (0.2 or less), high sulfur slags (6-8%) will be sufficiently fluid to readily pour from the combustor and at the same time exhibit high enough viscosities to minimize refractory wear. For this reason the bulk of experimental combustor work was conducted using slags at 0.2 basicity. The addition of coal to the combustor would add sufficient ash to the yield slags in the range of 0.1 to 0.2 basicity.

SULFUR PARTITION BETWEEN IRON AND SLAG

Introduction

In the two-stage coal combustion process, sulfur is introduced into the iron bath of the combustor that is injected beneath the molten surface. From an economic point of view, it is desirable that all of the coal sulfur be recovered from the iron bath as calcium sulfide in the molten slag. The distribution of sulfur between the liquid slag and the molten iron at steady state is of primary importance. This distribution (termed the partition ratio) is defined as the ratio of the percentage of sulfur found in the slag to the percentage of sulfur in the iron.

For optimum operating conditions, it is desirable that the partition ratio be as high as possible. In this manner, the bulk of the sulfur will be present in the slag rather than in the iron phase. If a high partition ratio (10 or more) can be obtained with relatively low excess lime, the lime consumption will be low and operating costs will be reduced. Furthermore, as the partition ratio increases, the sulfur content of the iron decreases which results in a higher value for the iron produced in the process.

Based on the literature available for partition ratios of blast furnace and steelmaking slags, high partition ratios are associated with increased temperature, a reducing atmosphere and high slag basicity. However, these data are generally confined to slags containing less than 2 percent sulfur. Unlike steel manufacturing processes, the combustor will operate with slags containing large amounts of sulfur (about 8 percent). The only partition ratio data available for such high sulfur slags were developed for high basicity magnesia-bearing slags[2].

Accordingly, a laboratory investigation was initiated to determine the partition ratios and sulfur content for both the iron and the slag when a low basicity high sulfur bearing slag (calcium oxide-silica-alumina system) was in contact with molten iron. Although data are not available to determine the effect of free calcium sulfide on partition ratio, no attempt was made to measure the maximum solubility of calcium sulfide in these slags. Rather, a study was made to evaluate the overall effect of high-sulfur slags (regardless of solution state) on equilibrium sulfur partition ratios.

In this series of experiments, the equilibrium partition ratio was obtained by transferring sulfur from the slag to iron, rather than from the iron to the slag as expected to occur in the process. This was done to save cost and time, since this approach was proved valid by the data obtained from a previously completed study[2] which showed that equilibrium was reached by either method.

Experiments were divided into two groups. The first group involved the determination of the minimum time required to reach partition equilibrium. The second group was concerned mainly with the effect of temperature and slag basicity on sulfur partition ratios.

Slag Preparation

In this investigation, synthetic slag samples were prepared by mixing master batches of CaO, SiO_2, Al_2O_3, and CaS to obtain slags of varying basicity as shown in Table VIB.

TABLE VIB

Slag Composition for Partition Ratio Studies

Basicity	CaO	SiO_2	Al_2O_3	CaS
0.2	13.4	44.4	22.2	20.0
0.5	26.0	36.0	18.0	20.0
1.0	40.0	26.6	13.3	20.0

These mixtures were then placed in graphite crucibles and heated to 2600°F - 2760°F for at least eight hours. Each crucible was removed from the furnace, stirred and returned to the furnace. The stirring was repeated at least twice to provide a uniform slag composition. The slag was then removed from the furnace, cooled and crushed to minus 10 mesh U.S. These synthetic slags were used in all subsequent experiments.

Effect of Time and Temperature on Approach to Equilibrium

A Burrell Model H-2-9 high-temperature electric furnace was used for this work. The furnace, which contains two heating chambers (1-1/2 inch ID combustion tubes), was placed on its side so that the chambers were in a vertical position. The bottom openings of both heating chambers were sealed except for a gas inlet.

A silicon carbide rod was placed in an upright position in the bottom of each chamber and served as a base for small graphite crucibles containing crushed iron covered with a granulated slag. At the start of the experiment, the heating chambers were heated to test temperature and flushed with

nitrogen through the gas inlet at the bottom of the chamber for at least 10 minutes. Two small crucibles, one on top of the other, were placed in one of the heating chambers. The crucibles (3/4 in. ID x 2 in. high) contained 6 grams of iron and 1.5 grams of slag. A larger crucible (3/4 in. I.D. x 3 in. high) containing 12 grams of iron and 3 grams of slag was placed in the other chamber. Aluminum foil was installed inside each heating chamber 1-2 inches down from the top to serve as a radiant heat reflector. The nitrogen flow was stopped when the rubber stoppers of both heating chambers were tightened. The heating intervals were measured from the time the furnace temperature reached 2600°F until the samples were removed. The heating times varied from 30 minutes to 24 hours.

The effect of time at temperature on the approach to equilibrium partition ratios is presented in Figure 9B. In these experiments, furnace temperature was maintained constant at 2600°F (sample temperature estimated at 2450°F). Initially, when all of the sulfur is in the slag, the partition ratio is infinite. However, as the slag and molten metal are held in contact, the partition ratio rapidly decreases and slowly approaches an equilibrium value after 10 hours. The data scatter is typical of what one may expect from measurements of this sort. However, it is interesting to note that the data are independent of the type of crucible used as well as the position in the furnace. Based on these results, it was decided that in subsequent work for determining the effect of basicity ratio and sulfur content on expected partition ratios, the contact time should be maintained at 10 hours.

Effect of Slag Temperature and Basicity on Equilibrium Partition Ratio

To expedite the work, the second group of experiments were completed in the laboratory-constructed viscosimeter furnace. This furnace has a cavity of 8 inches wide by 9 inches long by 8 inches high. A refractory crucible holder with 5/8 inch diameter 1 inch deep holes to accommodate six graphite crucibles and a thermocouple was placed in the furnace and was heated to a predetermined temperature with an argon purge for at least 1/2 hour prior to installing test samples. The test samples, consisting of approximately 0.9 grams of slag and 3.6 grams of iron granules (containing 4 percent carbon), were contained in graphite crucibles approximately 1/2 inch OD and 3/8 inch ID by 2 inches long. The slags in this work were the same as those listed in Table VIB.

After the crucibles were placed in the crucible holder, charcoal or graphite powder was sprinkled over the entire assembly and a stream of argon was maintained in the furnace to prevent disintegration of the graphite crucibles by air infiltration. The samples were maintained at a specified temperature for ten hours to insure equilibration. The temperature was measured at the center of the crucible holder. The entire contents in each crucible were crushed and separated into magnetic (iron)

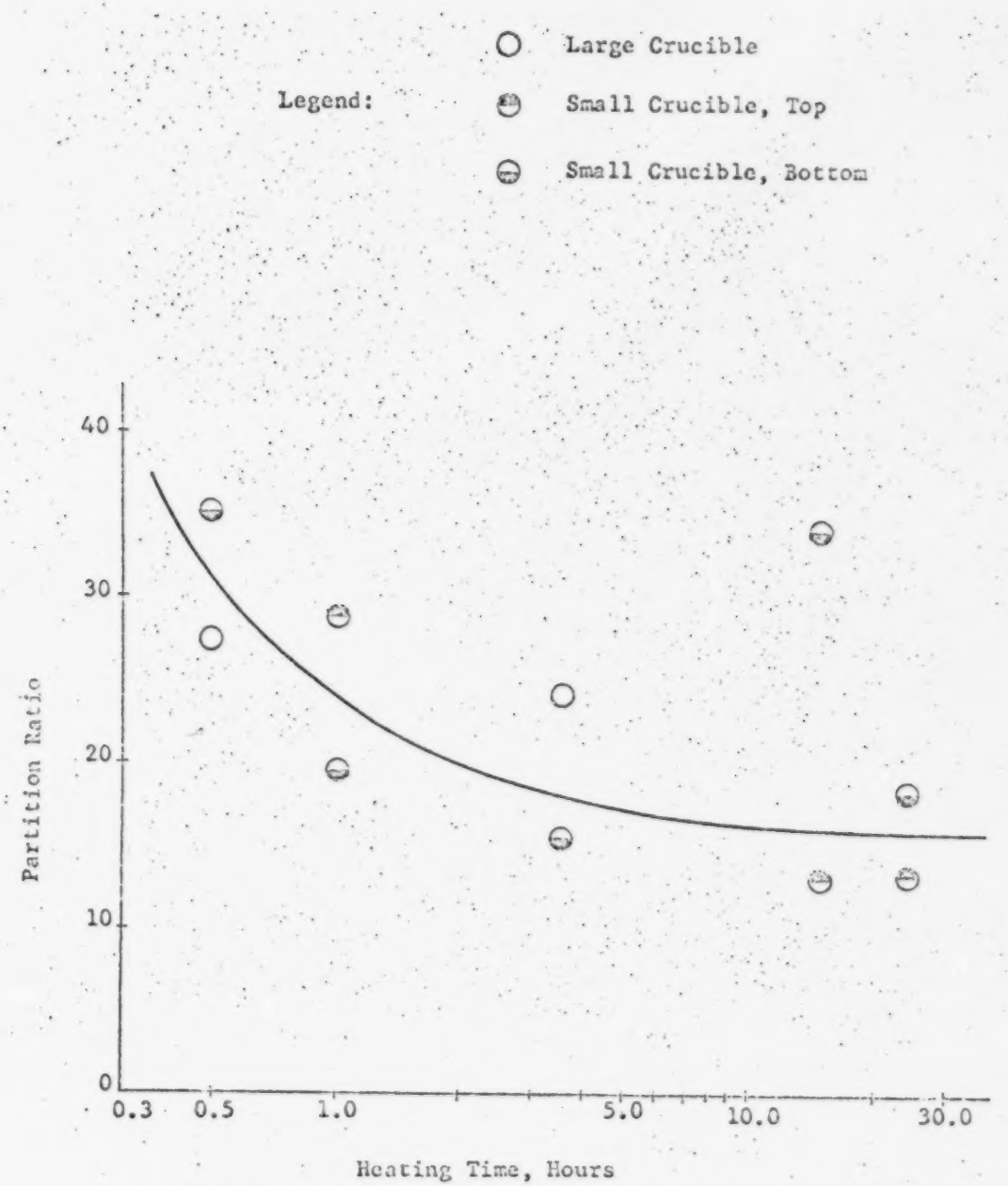


FIGURE 9B-EFFECT OF HEATING TIME ON PARTITION RATIO

and non-magnetic (slag) portions and the sulfur content of each portion was determined.

Figure 10B presents the effect of slag temperature and slag basicity on the equilibrium partition ratio that is achieved. The data show that the partition ratio for a given slag basicity rapidly increases with increasing temperature. It should be mentioned that, unlike the temperatures in Figure 9B which were furnace temperatures, the data of Figure 10B are based on actual slag temperatures. Because the combustor economics are vastly improved when using slags of 0.2 basicity or less, the partition ratio data are encouraging in that high values can be realized even though low basicity slags are employed. The data show that, for a 0.2 basicity slag, partition ratios of the order of 25 to 170 may be realized over the temperature range of 25-2700°F. The latter temperatures span the operating temperature that will be achieved in the combustor operation.

HEAT CAPACITY

Introduction

Heat capacity data for the various slags at high temperatures are required to adequately define the heat balances for the process. This section presents the results of work done on three different types of slags having basicities of 0.2, 0.5 and 1.0 (Table VIB). These slags were selected as typical of those that may be used in the operation of the combustor.

Procedure

Standard calorimetry equipment and procedures were used to determine the specific heat of solids. The calorimeter was a one-liter capacity Dewar vacuum flask. To preclude the possibility of slag reaction with water, ethylene glycol was used as the heat absorption liquid. Specific heat data on the laboratory C.P. grade of ethylene glycol used were obtained from the literature[15]. A Beckman differential thermometer graduated to 0.01°C and capable of interpolation to 0.005°C was used to measure the temperature rise of glycol. A standard laboratory thermometer accurate to within 0.5°C was used to measure the absolute end point temperature of the glycol and cooled solids.

Before beginning experiments, the heat absorption values for the Dewar flask calorimeter, Beckman thermometer and stirrer were determined. A cork stopper was used to cover the Dewar. The Beckman thermometer and stirrer were introduced into the flask through holes punched in the cork. The calibration of the Dewar flash for heat absorption and losses was done by in-situ neutralization of sulfuric acid with sodium hydroxide. The heat input or theoretical heat of reaction due to neutralization was obtained from the literature[16]. The difference in literature and experimental values was the heat absorbed by the calorimeter.

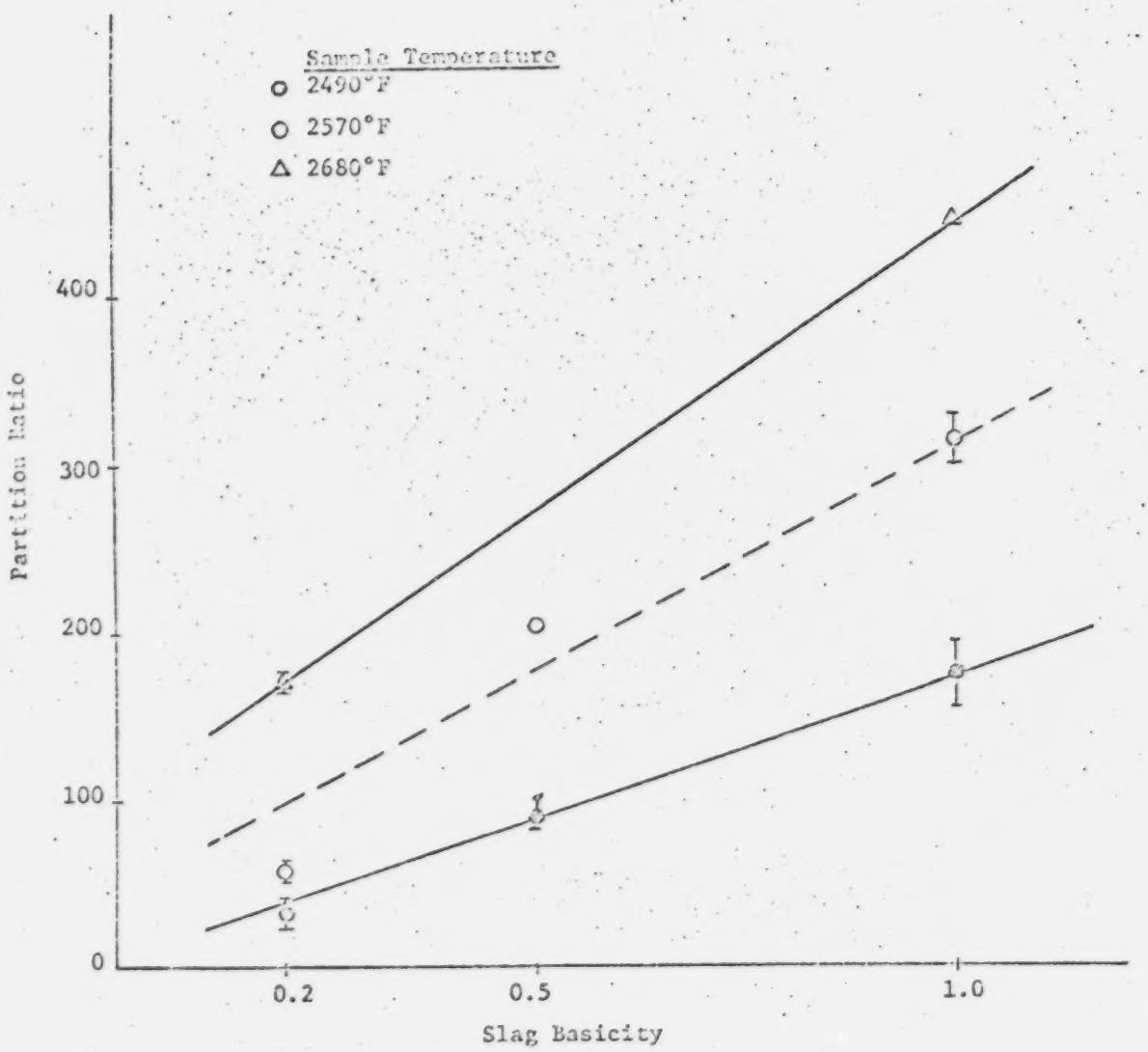


FIGURE 10B- EFFECT OF SLAG BASICITY ON PARTITION RATIO

Once the calorimeter constant was evaluated, the method was standarized by determining the specific heat of aluminum and nickel over the temperature range 300 to 1200°C. A comparison of the experimental and literature values for the specific heats of aluminum and nickel permitted an estimate to be made of the heat losses experienced during the transfer of the hot aluminum or nickel sample from the furnace to the calorimeter. The difference in the heat content measured and that calculated from the literature values for the specific heat of both materials was attributed to radiant heat losses as well as glycol evaporization. Correction factors were developed which related the difference in measured and literature heat content values through the emissivity and surface area of the sample. These corrections are shown in Figure 11B as a function of initial sample temperature.

For determining the specific heats of the various slags, the following procedure was used. Slag samples were briquetted into a cylindrical disc of 1 inch diameter and 1/8 inch thick. The slag disc was then inserted into a ceramic combustion thimble and both were heated to temperature in a muffle furnace. The weight of the thimble varied between 60 and 70 grams and the ratio of thimble to slag sample weight varied between 4 and 8. Relatively massive thimbles were used to minimize heat losses from the slag disc during transfer from the heatup furnace to the calorimeter.

The calorimeter containing a known weight of glycol (usually 500 grams), was allowed to equilibrate with the surroundings. The Beckman differential thermometer was adjusted to read near the bottom of the scale so that a maximum temperature increase (5.2°C) in the glycol could be measured. In the event that the temperature rise of the glycol exceeded the range of the thermometer, the test was discarded. Once the differential thermometer had been standardized, the combustion thimble containing the slag briquette was removed from the heatup furnace. The temperature of the combustion thimble and slag sample were continuously monitored by means of a thermocouple inserted within the thimble. Upon removing the thimble and briquette from the furnace, the briquette was immediately transferred to the calorimeter by simply dumping the contents of the thimble. During the dumping of the slag briquette, glycol fluid agitation was maintained by means of a glass stirrer. The temperature of the glycol was measured by means of the differential thermometer as a function of time. Measurements were continued until a constant rate of cooling of a glycol was observed. In this manner, heat capacity data could be corrected to account for heat losses from the system. It should be mentioned that these corrections were relatively small. The effect of calorimeter heat losses on the measured specific heat was less than 0.1 percent.

Results

The effects of slag basicity and temperature on the heat content (above 28°C) of various slags are presented in Figure 12B. As can be seen, slag basicity has little or no effect on the enthalpy of the solids.

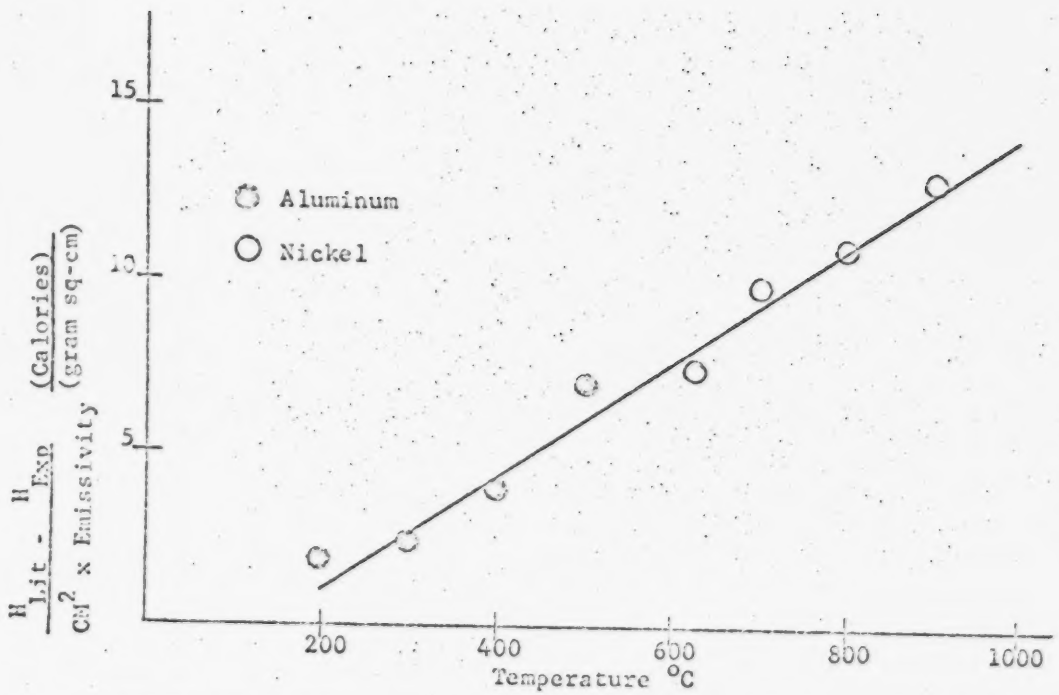


FIGURE 11B-CORRECTION FACTOR FOR HEAT LOSSES DURING SAMPLE TRANSFER TO THE CALORIMETER

Within the limits of experimental data, all of the slags exhibit similar characteristics. The data of Figure 12B were correlated by means of a least square polynomial fit. For comparison purposes, the correlating curve is shown along with a heat content curve for open hearth and blast furnace slags[17]. As is evident, the high sulfur bearing slags used in this work exhibit characteristics not too far removed from those of commercial blast furnace and open hearth slags.

To obtain the heat capacity of the various slags, the polynomial expression correlating the enthalpy with temperature was differentiated with respect to temperature. The derivative, which is defined as the heat capacity, is presented as a function of temperature in Figure 13B. A comparison of the experimental values for the combustor slags with those of open hearths and blast furnace slags indicates that the materials are somewhat comparable in nature. The high sulfur slags tend to exhibit a somewhat higher heat capacity.

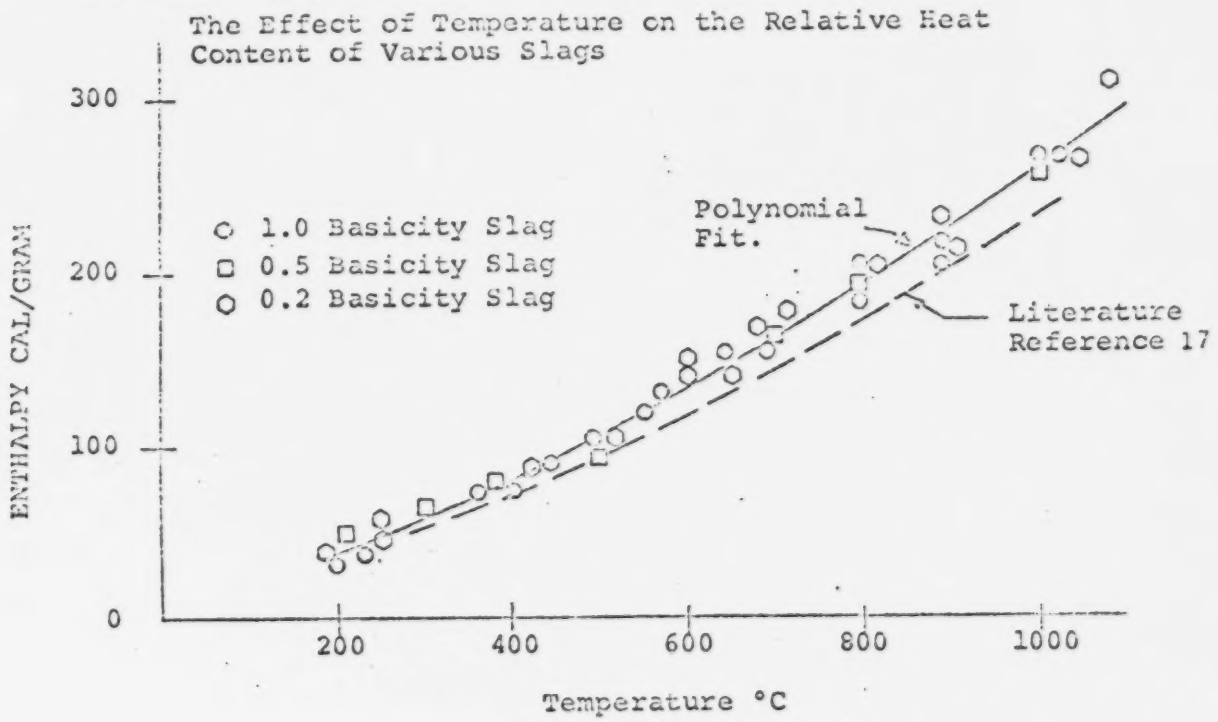


Figure 12B

The equation correlating the heat capacity as a function to temperature is as follows:

$$Cp = 0.119 + 3.66 \times 10^{-4} T - 15.90 \times 10^{-8} T^2$$

where Cp is in calories/gram/degree C. It is valid for temperatures between 200°C and 1200°C and slag basicities between 0.2 and 1.0.

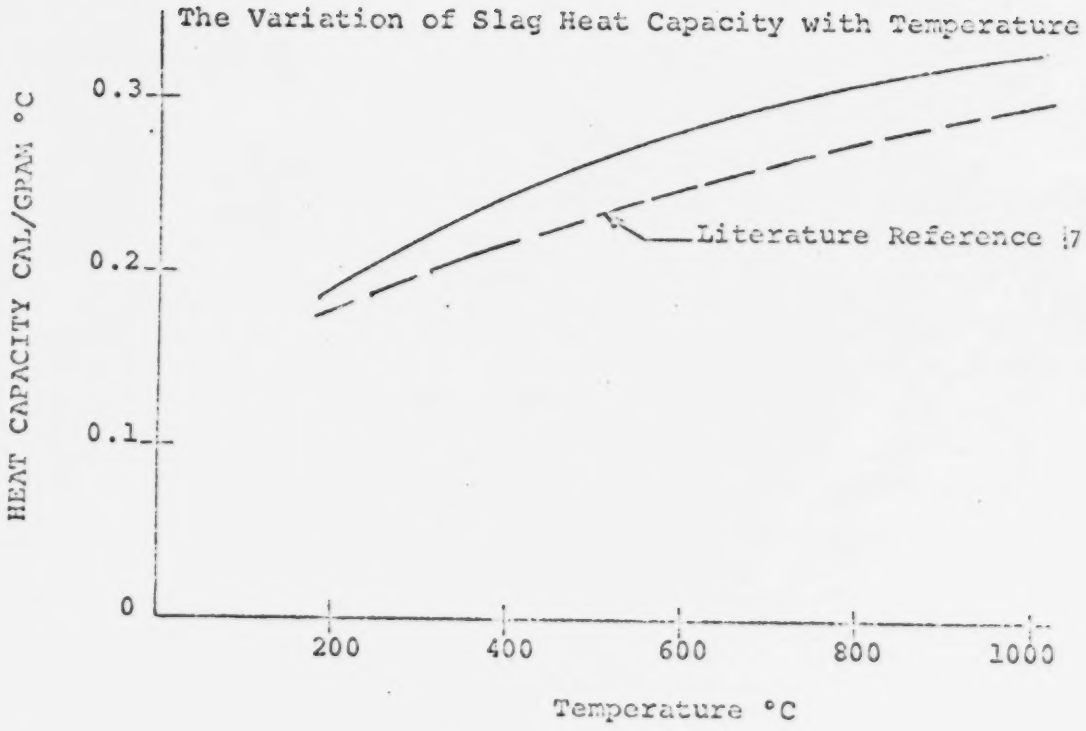

The Variation of Slag Heat Capacity with Temperature
HEAT CAPACITY CAL/GRAM °C
0.3
0.2
0.1
0
Literature Reference 17
200
400
600
800
1000
Temperature °C

Figure 13B

Total Specific Surface Area

One of the measurements of the physical properties of high-sulfur bearing slags required as a possible correlating variable for the desulfurization and granulation studies on such slags is their total surface area. Tests were conducted on three slags of 0.2, 0.5, and 1.0 basicity ratio (basicity defined as percent of calcium oxide divided by percent silica plus percent alumina). The composition of these slags is shown in Table VI-B. A Perkin-Elmer 212D Model Sorptometer was employed for these measurements.

Procedure

The principle of the surface area measurement is based on the amount of gas absorbed by a solid sample. In this method, a known mixture of nitrogen and helium is passed over the sample (1.0-2.0 grams) in a sample tube and the effluent is monitored by a thermal conductivity detector. While the gas is flowing through the tube containing the sample, the tube is cooled by immersion in a bath of liquid nitrogen. As a result, the cooled sample adsorbs a certain amount of nitrogen from the gas stream, which is indicated on a recorder chart as a peak. The area of this peak is proportional to the volume of nitrogen adsorbed by the sample. After equilibrium is established, the sample tube is removed from the liquid nitrogen bath. As the sample warms the adsorbed gas is released and enriches the effluent gas passing through the sample tube. A desorption peak is then obtained, which is in the reverse direction of the adsorption peak. When desorption is complete, a known volume of nitrogen is added to the nitrogen-helium stream to produce a calibration peak. By comparing the areas under the desorption and calibration peaks, the volume of the nitrogen adsorbed by the sample can be calculated.

Discussion of Results

Prior to measuring the total surface area of the slags, the sorptometer was standardized by measuring the surface area of a calibration sample. A standard sample of Titanium dioxide (TiO_2) supplied by the American Instrument Company was used for this work. The known total surface area was 10.3 $\pm$ 0.2 square meters per gram. Excellent agreement was found between the standard sample surface area and that determined by means of a sorptometer. The experimental value was 10.67 square meters per gram.

The results of surface area determination on the three different basicity slags are shown in Table VII-B.

TABLE VII-B

Total Surface Area of High Sulfur Bearing Slags

Basicity	Surface Area SQ. M/gram
0.2	0.3
0.5	less than 0.1
1.0	less than 0.1

As is evident from this table, only the 0.2 basicity slag exhibited a sufficiently high surface area for meaningful measurements. The outer two slags had surface areas too low for measurement by the sorptometer, which can measure surface areas down to 0.1 square meters per gram. The surface area shown for the 0.2 basicity slag represents an average value for five different measurements. The average specific surface was 0.31 square meters per gram and the range of the experimental data was from a low of 0.20 to 0.43 square meters per gram. Variability in the measured surface areas was attributed to variations in slag composition. A number of tests were conducted on the other two slags; however, surface areas were outside the range of the instruments.

Because the slags are glass-like in nature, it can be expected that the total surface areas will be minimal. In particular, because the higher basicity slags tend to be more glassy, total surface areas decrease with increasing basicity.

EXTERNAL SURFACE AREA

Introduction

As part of the detailed slag characterization, the external specific surface area of slags over the basicity range of 0.2 to 1.02 was determined. The external specific surface is a useful correlating variable for subsequent work, such as slag desulfurization reaction kinetics and slag surface expansion by granulation and is necessary to determine the grinding energy requirements for the various slags. This section presents the results obtained from the experimental investigation of the external surface areas of high sulfur bearing slags.

Theory

The relationship of the specific surface area of the solids to the pressure drop obtained in laminar flow of fluids through packed beds of granular materials had been formulated[10]. The theoretical expression relates the volumetric flow of fluids to the pressure drop established per unit length of bed, the specific surface of the solids, bed porosity, the viscosity of the fluid, and the cross-sectional area of the packed column. Since all variables with the exception of the specific surface are readily measured experimentally, the specific surface can be calculated from the following equation:

$$S = \frac{14}{d} \left(\frac{E^3}{(Pv\ (1 - E)^2)} \right)^{1/2}$$

where **d** = the apparent density of the solids, grams/cubic centimeter
E = porosity, dimensionless
v = kinematic viscosity of fluid, square centimeters/second
S = specific surface, square centimeters/gram
P = permeability of packed bed, centimeters/(second)^2

If laminar flow of fluid is maintained throughout the packed bed, the above equation adequately describes the relationship between the measured variables and the specific surface area. Data reproducibility can be maintained within plus or minus 10 percent.

Equipment and Experimental Procedure

The apparatus used to measure the specific surface[18] consisted of a flow meter, an inclined manometer, and a volumetrically graduated sample holder of known cross-sectional area. To determine specific surface of the slags, it is required that the apparent density of the slag particles be known. An apparent density measurement, rather than a true solid density determination, is required because the latter value is independent of the porosity, or pore volume, of the particle. Since fluid flow does not occur within the particle, it is necessary that the apparent density be used to evaluate the open porosity of the bed. Apparent densities were determined by total immersion of the slag particles, and the density and the volumetric displacement of the carbon tetrachloride by the slag particles, the apparent density was readily calculated.

The experimental procedure for determining the specific surface was as follows. A weight of solids of known apparent density was poured into a graduated glass sample tube holder and vibrated to maximize the packing of the solids. Knowing the length of the packed bed and the cross-sectional area of the sample tube holder, the sample volume was then calculated. Bed porosity was determined from the weight, density, and the volume of the packed bed. Once the bed parameters were measured, a known volume of air was caused to flow downward through the bed. The pressure drop across the packed bed was measured when steady flow conditions had been achieved. In general, pressure drop measurements were obtained for at least five different air flow rates.

For the equipment used in this work, an air flow rate of five cc per second or less insured a laminar flow condition. For laminar flow, a plot of pressure drop versus the volumetric flow rate yields a straight line passing through the origin. The slope of the straight line represents the permeability of the bed. Using this permeability value along with the viscosity of the air, the porosity and apparent density of the solids, the specific surface was calculated by the equation presented earlier.

Discussion of Results

Earlier work[18] established the validity of the specific surface area measurement. In that work, glass beads having nominal diameters of 3, 4, and 6 milimeters were employed. The specific surface of the glass beads was determined by micrometer measurements of the diameter and by obtaining a particle count per unit weight for the different size glass

beads. In this manner, the specific surface in terms of square centimeters surface area per gram of sample was determined. A comparison of the surface areas obtained by the micrometer measurement and air permeability methods is presented in Table VIII-B. Agreement between the two methods was excellent.

TABLE VIII-B

Comparison of Glass Bead Surface Area Measured by Micrometer and By Air Permeability Method

Glass Beads Diameter, mm	Specific Surface, sq cm/gram	
	Air Permeability	Micrometer
3.15	7.4, 7.7, 7.9	7.6
4.06	5.5, 5.8, 6.1	5.9
5.95	3.9, 4.1, 4.4	4.1

The effect of basicity and particle size on the external specific surface area of slags shown in Table VI-B is presented in Figure 14-B. The data show that the specific surface rapidly increases with decreasing particle size. Scatter in the data is attributed to variation in the sampling and composition uniformity of the slag. Because calcium sulfide has a limited solubility in lime-silica-alumina slags, it is probable that the fracture characteristics of the particles are highly dependent upon localized concentration of segregated slag components. No significant differences could be observed between slags of 0.2, 0.5, and 1.0 basicity. For comparison purposes, the smoothed curve obtained for magnesia-lime-silica-alumina slags containing about 18 percent calcium sulfide is also shown in Figure 14-B. These data were obtained for completed work for the Water Quality Office[2]. Evidently, since the slags are glass-like in nature, the fracture characteristics tend to generate similar external surface areas which are relatively independent of compositional changes. The crushing energy requirements also tend to substantiate this conclusion.

CRUSHING ENERGY

Introduction

In the Two-Stage Coal Combustion Process, high sulfur bearing slags are periodically withdrawn from the combustor and processed to recover elemental sulfur. The molten slag may be granulated by means of water quenching and/or vacuum treatment to produce a particulate material. Alternatively, depending upon process designs parameters, the slag may be cooled in molds and subsequently ground to produce a size distribution that would optimize process economics. Slag particle size influences the desulfurization equipment size and the commercial utility of the coarse road aggregate produced. Regardless of the process employed to

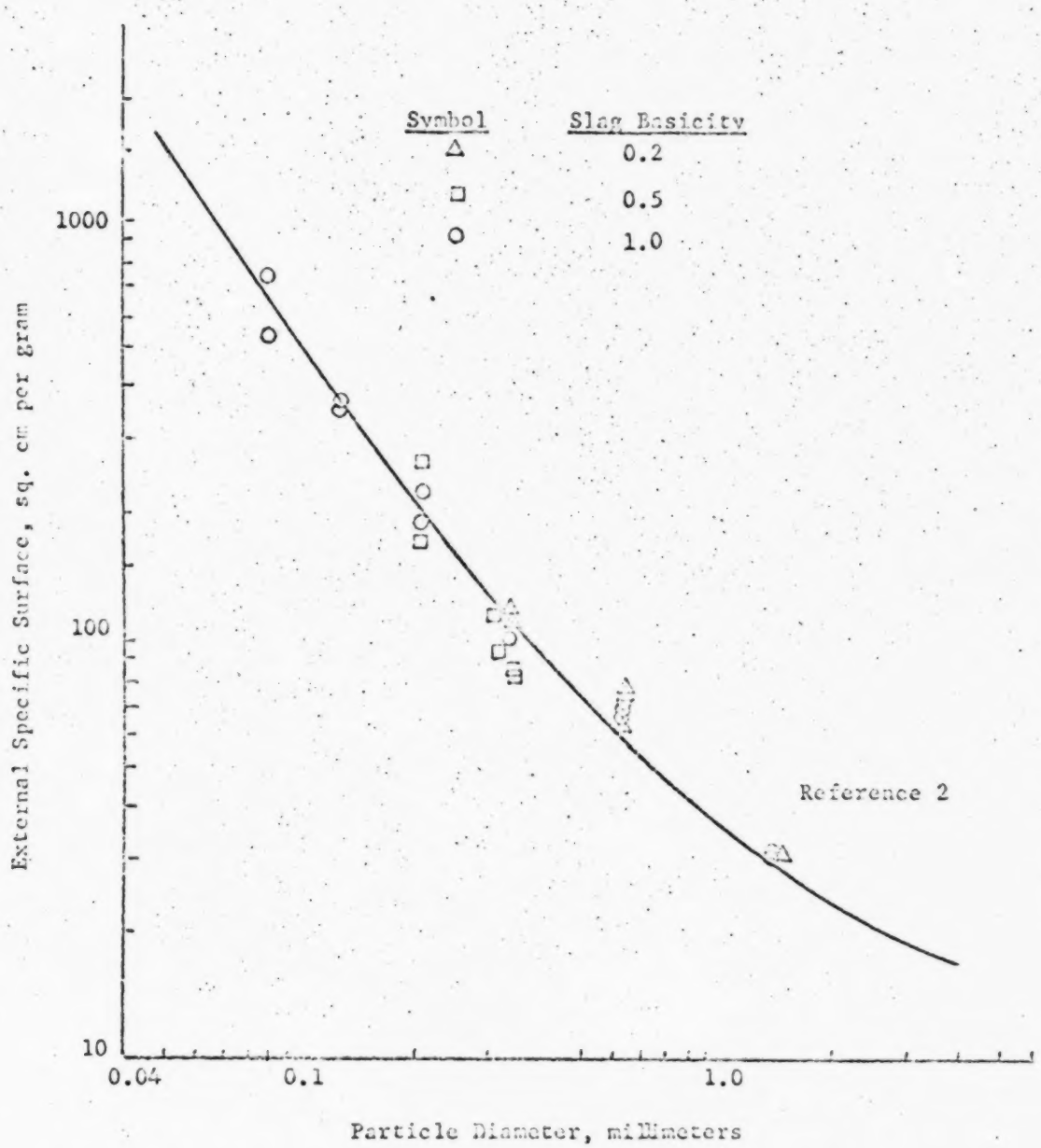


FIGURE 14-B-EFFECT OF SLAG BASICITY AND PARTICLE SIZE ON EXTERNAL SPECIFIC SURFACE

produce a particulate slag material, the possibility exists that crushing and grinding equipment will be required. Because both the capital and operating costs for crushing equipment depend on the crushing energy required to produce the particle size of the slag, a study of crushing energy requirements was undertaken.

Experimental Equipment and Procedure

A modified version of the drop-weight machine used by Gross[19] was used in this work. A schematic diagram of the equipment is presented in Figure 15-B. A stainless steel cylindrical split die and stainless steel plunger comprised the assembly that housed the slag crushing chamber. The crushing chamber (6.1 cm diameter) consisted of a cavity formed by the volume of the slag contained between the bottom of the plunger and the upper surface of the die base. A 2.62 kilogram drop-weight was used to generate the energy required to crush the slag. The walls between the plunger and die were lubricated with graphite to minimize plunger friction.

A known weight (about 15 grams) of closely sized (minus 10, plus 20 U.S. mesh) slag was introduced into the die. The external surface area of a given slag sample was previously measured. The plunger is carefully inserted in the die and slowly lowered to rest on top of the bed of solids. The assembled die containing the slag sample rests on a circular piece of aluminum wire (0.064 diameter) and is centered directly beneath the drop weight. The aluminum wire had been previously calibrated to determine energy absorption as a function of wire diameter after deformation. The drop weight is raised by means of an overhead pulley to a known height above the plunger resting on the test solids. Once the elevated drop weight stops oscillating, the string is cut to permit the hemispherical drop-weight to impact on the center of the plunger. After impact, the aluminum wire is removed from beneath the die and measured in seven locations to determine wire deformation. If the deformation was not uniform along the entire length of wire, the test was discarded. Uneven deformation is the result of an off-center hit with the falling drop-weight which gives rise to binding friction between the die and the plunger. Consequently, the energy absorbed by the crushed solids is not known. When a uniform deformation of the wire is observed, the energy absorbed by the impacted solids is readily calculated as the difference of the energy input of the drop-weight minus the energy absorbed by the wire.

The crushed solids are then removed from the die and weighed to determine weight loss, (usually less than 0.5 percent). The external specific surface area of the crushed solids is then measured to determine the increase in surface area after crushing. Knowing the new surface area generated and the energy absorbed by the solids, the crushing energy, or Rittinger's Number, is calculated.

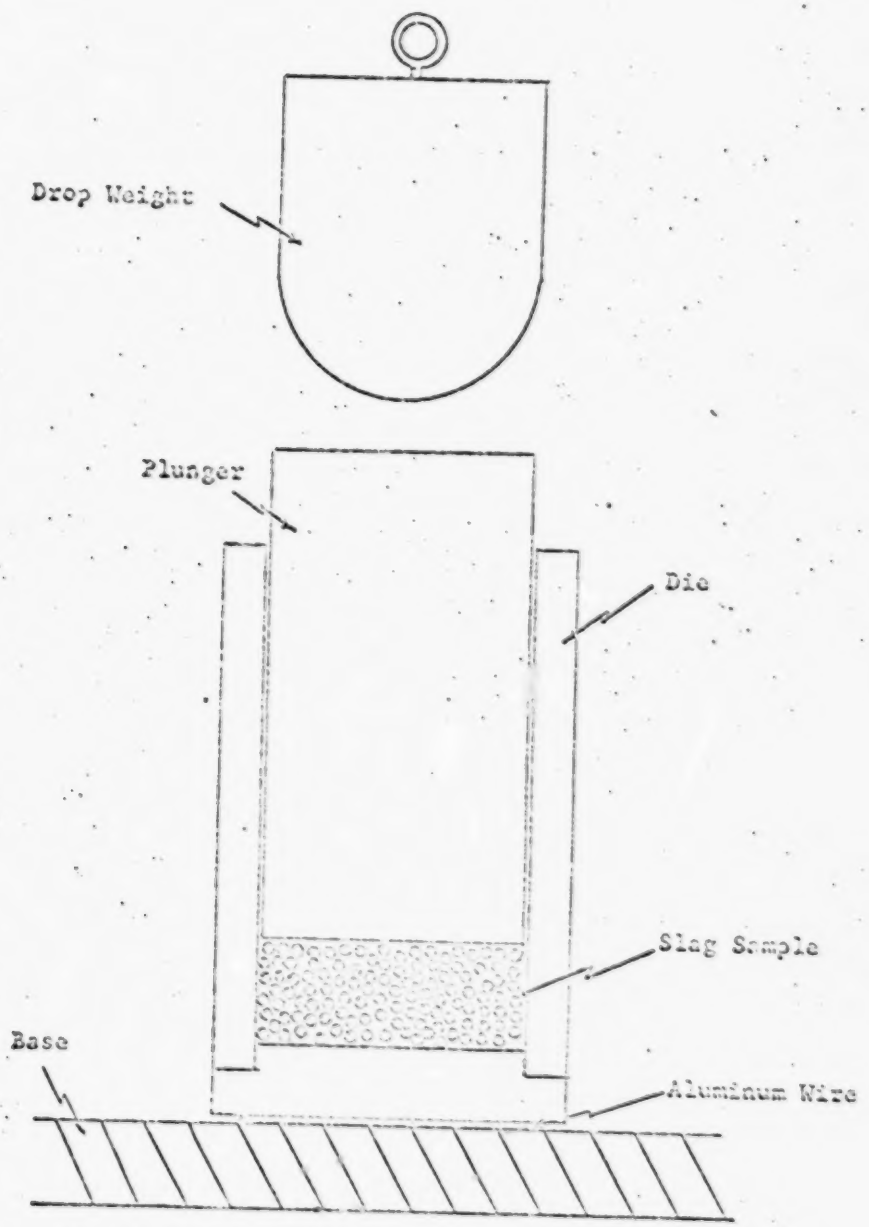


FIGURE 15-B- CRUSHING ENERGY APPARATUS

Previously developed[2] calibration curves which related the deformed aluminum wire diameter to the energy (kilogram centimeters) absorption were used in this work. The validity of the calibration curves were re-established at several different points. In these calibration experiments, no solids were introduced into the die. To obtain deformation data, the drop-weight was elevated to varying heights above the plunger and released. Prior experience has shown that alignment difficulties between the plunger and the drop-weight occur at high energy inputs and data reproducibility becomes poor. Accordingly, in these calibration tests and all subsequent experimentation, the drop-weight was not raised to an elevation greater than 15 centimeters. The results of the calibration tests are presented in Figure 16-B. As is evident, the data confirm the validity of the calibration curves.

Discussion of Results

The effect of slag basicity (over the range of 0.2 to 1.0) on the crushing energy requirements for slag containing 20 percent calcium sulfide are presented in Table IX-B. Chemical composition of the slags used in this work is shown in Table V-B. The data suggest that an optimum Rittinger's number is achieved at a slag basicity of 0.5. However, the extreme variability in the data limit the practical significance for the commercial application of the results. The difference between the results of the various basicity slags are not great enough to warrant a selection other than one common type of crushing and grinding equipment.

TABLE IX-B

Variation of Crushing Energy with Basicity

Basicity		cm^2/Kg-Cm Crushing Energy
0.2		
0.2		4.56
		2.12
		1.25
		1.72
		2.73
	avg	2.47
0.5		
		4.23
		2.96
		4.40
	avg	3.86
1.0		
		1.97
		1.49
		0.92
		3.39
	avg	1.94

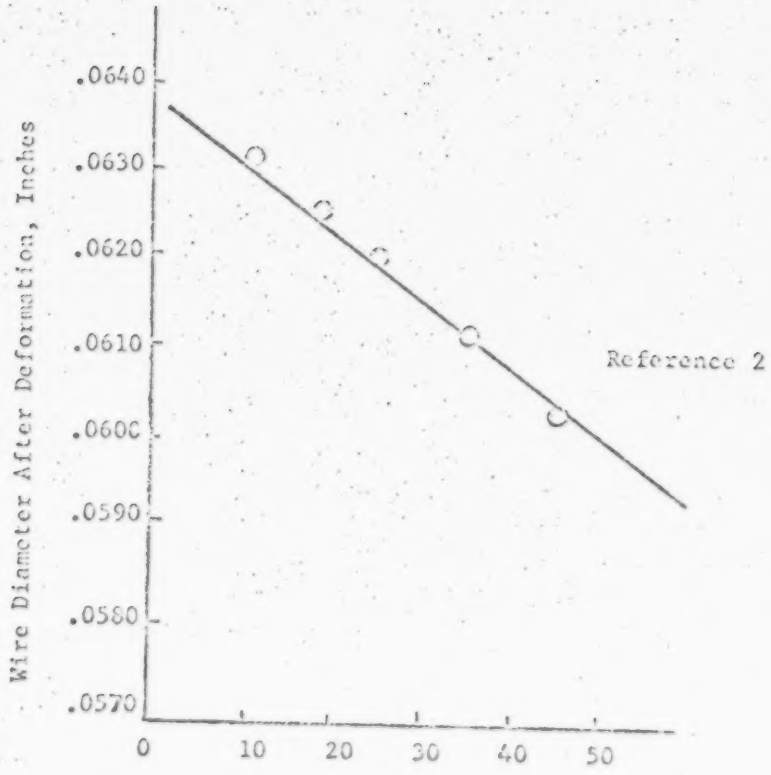


FIGURE 16B-CALIBRATION CURVE FOR ALUMINUM WIRE USED IN CRUSHING ENERGY TEST

The variability in the crushing energy results is attributed to the inclusion of undissolved crystalized calcium sulfide that is interspersed within the slag matrix. Calcium sulfide has a limited solubility in lime-silica-alumina slag system[20]. Depending upon the composition of the slag system, sulfur (in the form of calcium sulfide) solubility varies from 2 to 6 percent. In this work, the sulfur content of the various slags was about 9 percent. The excess of CaS in the slags creates a suspension of undissolved particles bound by a slag matrix. Since the cooling rate of the slag was uncontrolled during preparation, a variety of crystal sizes can be generated which give rise to a large variability in the surface areas generated during crushing.

Rittinger's Number was determined for silica sand to obtain a reference point for comparison of slag on a relative grindability scale to a common material for which commercial crushing equipment is available. A comparison of the slag to silica sand is presented in Table X-B and shows that the crushing energy requirement for these slags compared favorably with that of silica sand. Consequently, the selection of commercial equipment can be based on silica sand characteristics.

TABLE X-B

Comparison of Crushing Energy Requirements for Silica and Slags

Material	Average Crushing Energy sq cm/Kg-cm
Silica	3.33
0.2 Basicity Slag	2.48
0.5 Basicity Slag	3.86
1.0 Basicity Slag	1.94

It is of interest to point out that Gross[19] indicates a Rittinger's Number of 17.56 for silica as compared to 3.33 reported in Table X-B. The discrepancy is the result of the method by which surface area was determined. Gross used a rate-of-solution method rather than an air permeability technique to determine surface area. The rate-of-solution technique yields higher surface areas because of solvent penetration into the interstices of the particle. Air permeability measurements afford little opportunity for any significant penetration within the particle. Consequently, surface areas determined by the latter technique would tend to be low by comparison.

Rittinger's Numbers determined from measurements on commercial units[21] agree reasonably well with those obtained in this work. Literature values for the grinding of quartz in various sizes of ball mills range from 2.6 to 6.8 sq cm/Kg-cm as compared to the 3.33 value obtained. Based on the results of the crushing energy studies, the high sulfur bearing slags that will be produced in the combustor can be assumed to have grinding characteristics comparable to silica. This criterion should facilitate the selection of commercial equipment for use in the process.

GRANULATION STUDY

Introduction

As an alternative to slag crushing prior to desulfurization, a vacuum tower slag granulation technique was investigated. This granulation technique was studied because it is desirable to avoid the use of water in granulation because hydrogen sulfide formation is prevented and desulfurization heat requirements are lowered if the molten slag can be granulated without being cooled by contact with water

The proposed experimental technique involves the introduction of slag through a crucible into a vacuum shot tower which causes dissolved gases to leave and expand the slag; thereby, increasing the porosity and total surface area of the slag granules.

The purpose of this study was to determine if expanded slag particles could be produced by this vacuum tower technique and if so, to relate the orifice size in the crucible, the vacuum in the tower, and the slag temperature to the size, shape, and surface area of the slag particles formed.

Experimental Equipment

The concept behind increasing the surface area of slag granulated by the vacuum tower technique is simple. The objective is to form a small drop of molten slag at the bottom of an orifice and to expose this drop to a vacuum for as high a residence time as practical to enhance the opportunity for dissolved gases to escape from the slag droplet and create pores in the solidifying slag particle. Orifice size, slag flow rate, and temperature will affect the residence time requirement of the slag droplet at the orifice.

The experimental equipment is shown in Figure 17-B and consists of a 3 inch I.D. 15-foot steel pipe located on a sample collection box. At the column top is a flange on which concentric graphite crucibles were mounted. The crucibles had a hole (s) of known diameter and could be aligned to permit molten slag to flow through. Fittings on the collection box permitted the attachment of two vacuum pumps; a vacuum gauge was connected to the column. The slag was melted in the crucible using a carbon rod attached to an electric arc welding machine. Provision was made for an argon purge into the crucible to prevent the oxidation slag sulfur.

Prior to actual experimentation, a simulation study of drop formation was made using room temperature liquids which simulate molten slag. The experimental equipment is shown in Figure 18-B and consists of a vacuum flask connected to a vacuum pump. A fine orifice was fitted into a rubber plug and connected to a buret with a stopcock. In this manner, drop, bead, or stringer formation from an orifice of known diameter into a vacuum could be studied at room temperature.

Experimental Procedure

The procedure to study the formation of droplets in the flask involved setting the vacuum at the desired level (50 mm Hg) and introducing liquid

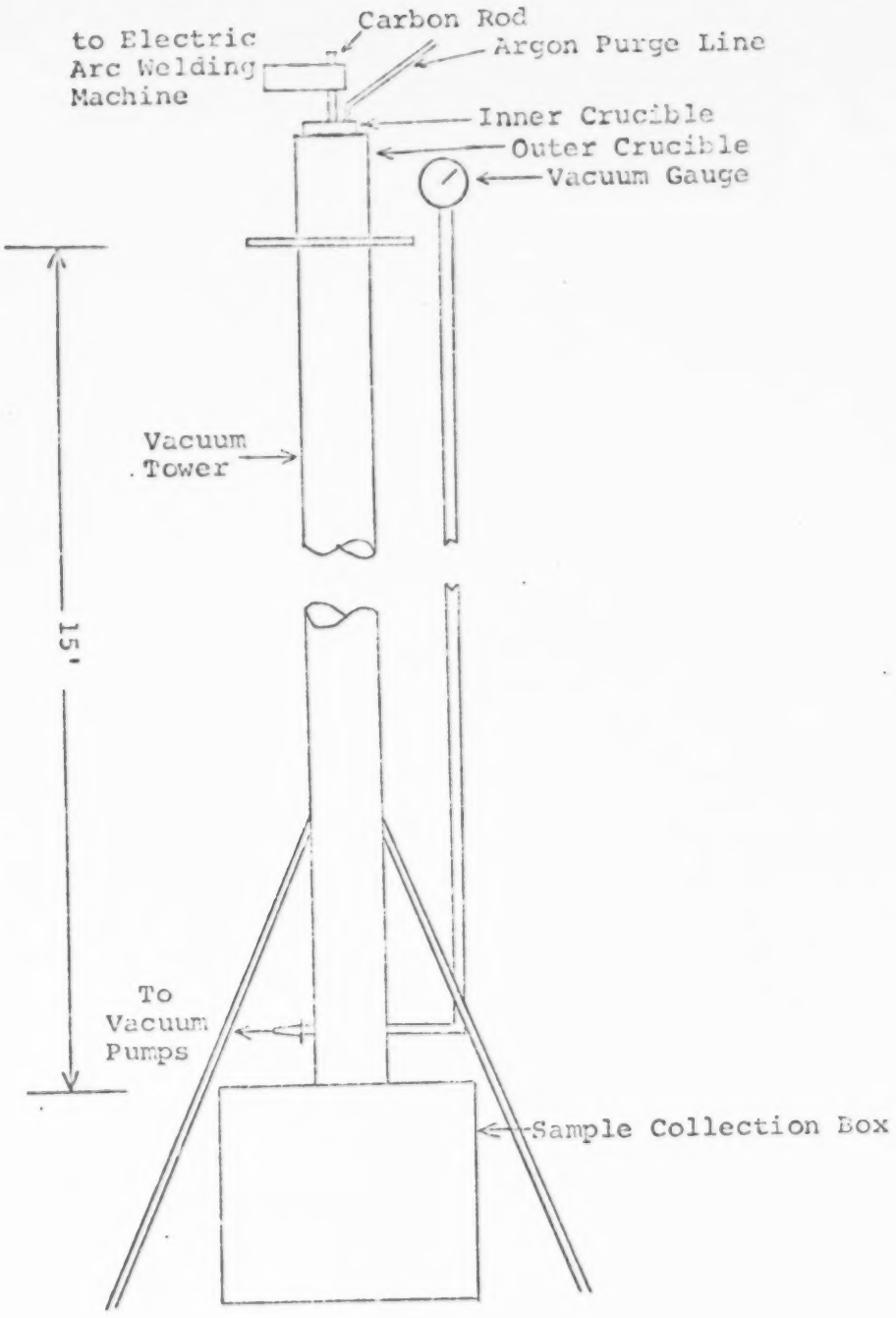


FIGURE 17-B -VACUUM TOWER GRANULATION APPARATUS

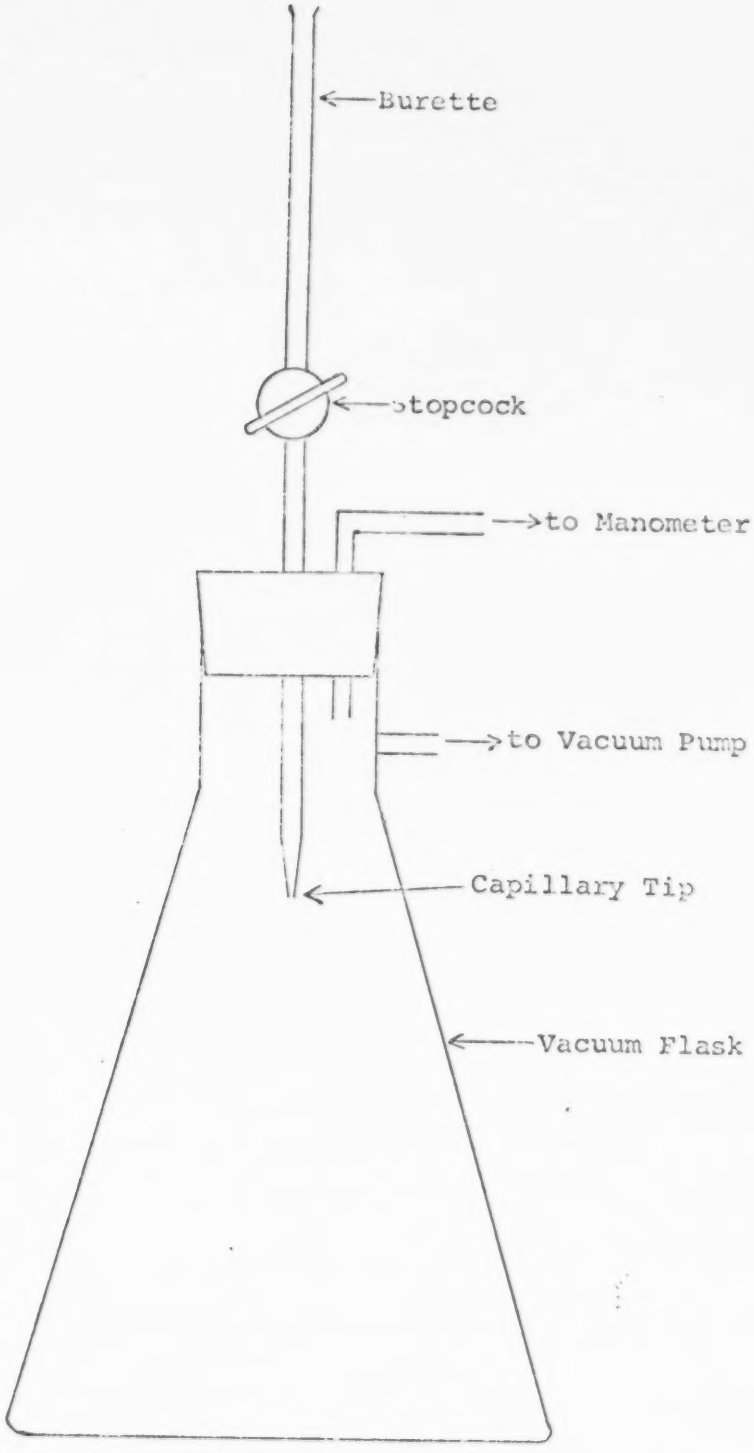


FIGURE 18-B - DROP FORMATION APPARATUS

from the buret through the stopcock. The formation of droplets or stringers could then be observed.

The procedure to operate the vacuum shot tower equipment was as follows. The crucibles, with holes misaligned, were cemented to the top of the tower. A sample collection pan, either dry or containing water, was placed in the sample collection box and the vacuum pumps started. When a vacuum of 28 inches of mercury was obtained, the inner crucible was charged with approximately 200 grams of slag and the carbon rod inserted in the slag. The electric arc was then started and the slag melted for 30 to 45 minutes with argon being purged into the inner crucible. When the slag was fluid, the holes in the crucibles were aligned and the slag was drawn into the tower by the vacuum. The granulated slag was collected in the sample collection pan. Several times during a run the temperature of the molten slag in the crucible was determined.

The total surface area of the minus 20 mesh fraction of the granulated slag was determined using a Perkin-Elmer Sorptometer; the external specific surface of the minus 10 plus 20 mesh fraction was determined using an air permeability technique[18]. The density of the minus 10 plus 20 fraction was measured by a liquid displacement technique. Particle size distribution for the granulated slag particles were determined.

Discussion

A qualitative comparison of the various shapes of granulated slag particles and their associated densities and surface areas is helpful in the evaluation of the granulation study.

(1) A solid sphere or bead should have the same apparent density as ungranulated slag. If it is assumed to be solid and smooth, its total surface area should be relatively low compared to crushed slag, which possess a certain amount of porosity and fissures from the crushing process.

(2) Long stringers would have the same characteristics as solid spheres. Both of these configurations are undesirable as compared to granulated slag particles because of their low surface areas.

(3) If conditions of residence time at the orifice, slag temperature and vacuum level in the tower are such that regular droplets (spheres) are not formed but irregularly shaped particles with rough surfaces, these latter particles should show an increase in specific surface area but no change in apparent density. If pore formation and honeycombing are negligible, the total surface area will be low.

(4) Spheres with open channels will have a different apparent density from ungranulated slag. Specific and total surface areas will probably be increased over ungranulated slag particles.

(5) Hollow spheres will have a decreased apparent density compared to ungranulated slag. The specific surface area should not change, while the total surface area may or may not change.

In the study of droplet formation in the vacuum flask, molten slag was simulated by a high viscosity oil and by liquid mercury. The physical properties of these two liquids are shown in Table XIB.

TABLE XIB

Physical Properties of Liquid Oil and Mercury

Liquid	Density (g/cc)	Viscosity Poise	Surface Tension dynes/cm
Oil (25°C)	0.87	50	26
Mercury (25°C)	13.5	0.015	480
Molten Slag (0.2 basicity, 8% sulfur, 2800°F)	2.5	50	480

The test was run under identical conditions (0.034 in. diameter orifice, 50 mm Hg pressure) for the liquids. The mercury would not form droplets but jetted through the orifice, while the high viscosity oil formed stringers of approximately 1 cm in length at a rate of approximately 1 per second. In the vacuum tower study, however, droplets could be formed from molten slag having the same surface tension as mercury but viscosity of approximately 100-150 poise resulting from operation at a temperature of approximately 2600°F. This drop formation was, therefore, accomplished with molten slag having a viscosity approximately 10,000 times greater than that of mercury through an orifice only three times the diameter of that used in the vacuum flask study. Because of the great differences in the behavior of the mercury and the slag having similar surface tensions but greatly different viscosities, it was concluded that viscosity was the controlling variable in droplet formation.

The results of the vacuum granulation study are presented in Tables XIIB and XIIIB and in Figures 19-B and 20-B. Figure 19-B shows the effect of orifice diameter on the total and external specific surface areas of the granulated slag produced in a 20 in. Hg vacuum from the molten slag at approximately 2600°F. As seen, both surface areas increase with increasing orifice size. Below one-sixteenth inch orifice diameter, it was not possible to obtain flow of the slag through the orifice. The increase of total surface area with increasing orifice diameter may be explained by an increase of the slag droplet residence time at the orifice which permits a greater opportunity for hot slag expansion to occur.

Although run reproducibility is poor, Table XIIB tends to indicate that the total surface area of the granulated slag is not a strong function of vacuum at an orifice diameter of 3/32 in. and a molten slag temperature of approximately 2600°F. On the other hand, the external surface area decreases with increasing vacuum at these same conditions. Introduction of the molten slag into the tower at atmospheric pressure produced slags

Table XIIB

VACUUM GRANULATED SLAG - EXPERIMENTAL RESULTS

Run No.	Vacuum (in. Hg)	Orifice Diameter (in.)	Temperature Range (°F)	Density (g/cc)	Specific Surface (cm^2/g)	Total Surface (m^2/g)	Sample Description
7-2-1	28	3/32	2440-2600	2.48	18.91	0.33	Stringers, beads, spheres
7-2-2	28	3/32	2500-2950	2.30	41.6	0.97	Beads, hollow spheres, filaments
7-12-1	17-21	3/32	2290-3240	2.39	57.42	0.41	Sandy, porous material
7-12-2	15-24	1/16	2340-2940	2.47	43.23	1.40	Sandy, porous material
8-2-2	7-16	1/8	2200-2490	2.30	53.39	9.13	Stringers, beads
8-3-3	0	1/4	2520-3240	1.85	72.71	<0.1	Small, porous, irregular particles
8-11-1	16-25	1/8	2250-2850	2.22	61.24	5.28	Stringers, beads, hollow spheres
8-11-2	8-12	3/32	2210-2980	2.41	44.45	0.40	Stringers, various size beads
8-12-1	17-22	3/32	2660-2910	2.37	36.02	1.91	Various size beads
8-12-2	26-28	3/32	2340-2720	2.21	38.62	1.26	Stringers, beads, hollow spheres
8-23-1	27	3/32	2300-3280	2.49	31.78	2.54	Stringers, beads, hollow spheres
8-30-1	9-18	3/32	2290-2930	2.35	48.80	0.42	Small beads, porous material
8-30-2	16-22	3/32	2280-2800	2.33	49.10	0.26	Small beads, porous material
(Original ungranul. slag)	--	-	----	2.55	----	0.38	-------

Table XIIIB

VACUUM GRANULATED SLAG - PARTICLE SIZE DISTRIBUTION

Run No.	Stringers	Weight Per Cents $+\frac{1}{4}$	$-\frac{1}{4}$ +6	-6 +10	-10 +20	-20
7-2-1	-	20.9	31.8	26.4	17.9	2.8
7-2-2 (beads)	-	22.1	38.8	24.5	14.5	0.1
7-2-2 (non-spherical)	-	14.8	66.0	17.3	1.7	0.2
7-12-1	-	--	30.7	11.7	43.5	14.1
7-12-2	-	--	3.0	45.0	51.0	1.0
8-2-2	8.6	--	4.2	22.5	48.9	15.9
8-11-1	11.4	--	5.0	22.3	40.0	21.3
8-11-2	1.4	2.7	5.1	30.8	44.2	15.8
8-12-1	0.5	--	4.4	31.5	47.6	16.0
8-12-2	2.5	6.7	17.6	29.9	29.8	13.6
8-30-1	-	1.7	2.5	19.0	57.8	19.0
8-30-2	-	--	9.9	17.3	51.6	21.2

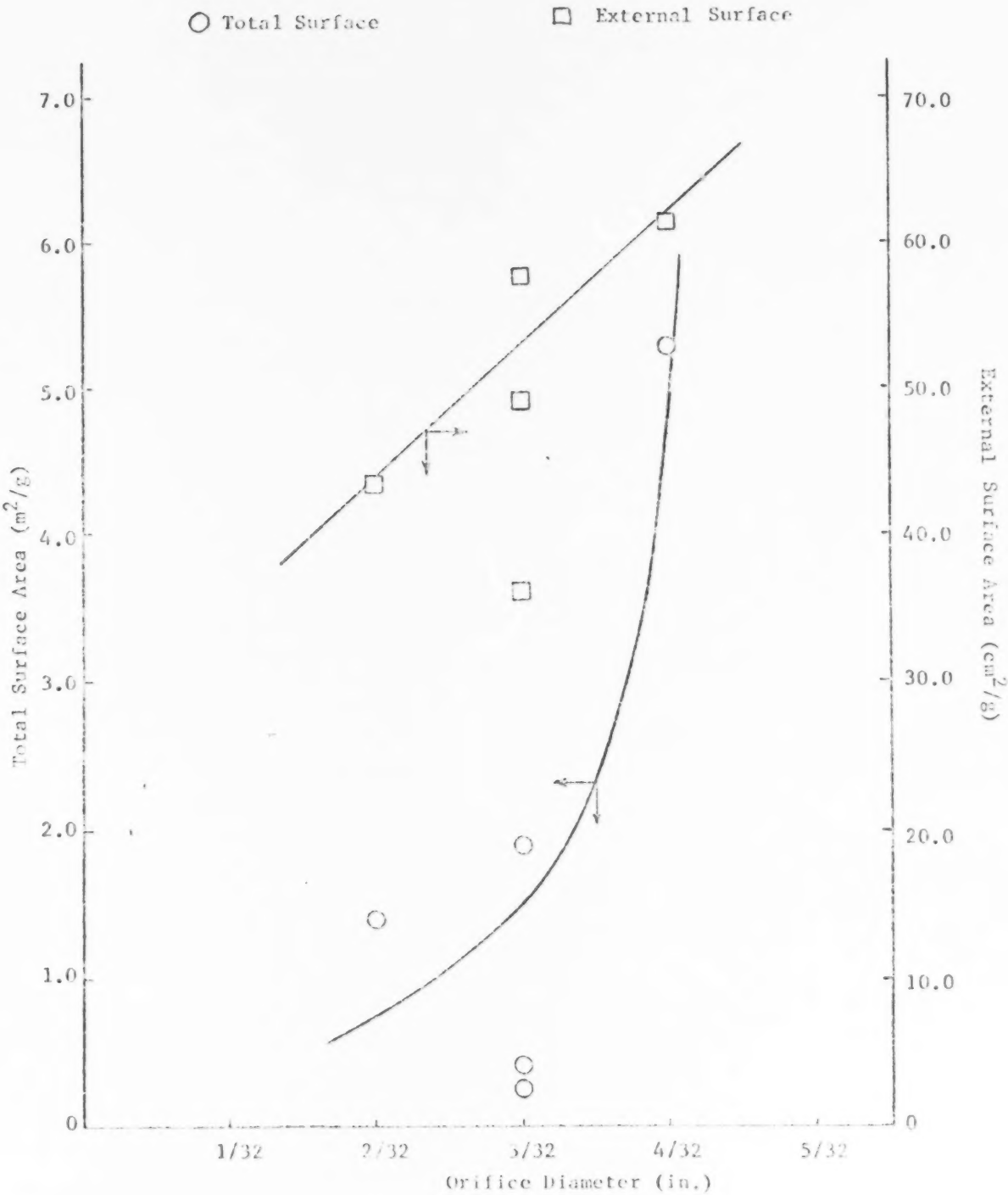


FIGURE 19-B-EFFECT OF ORIFICE DIAMETER ON SURFACE AREA OF GRANULATED SLAG (20 in. Hg Vacuum, 2540-2620°F)

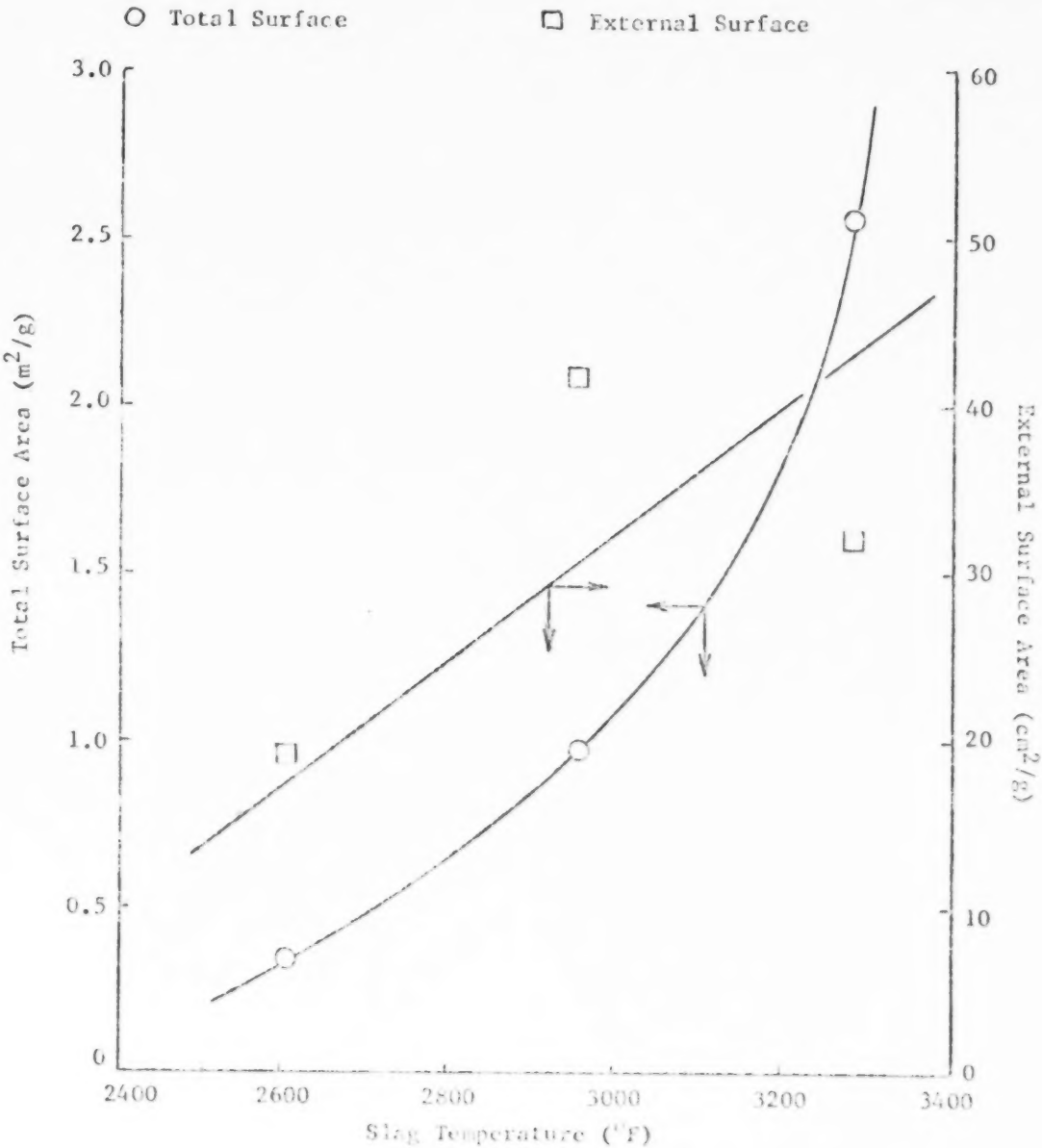


FIGURE 20-B-EFFECT OF TEMPERATURE ON SURFACE AREA OF GRANULATED SLAG
(3/32 in. Diameter Orifice, 28 in. Hg Vacuum)

of total surface area less than 0.1 m^2/g, that is, less than that of slags that have been crushed and ground (see Table XIIB). A possible explanation for this decrease may be surface sintering that sealed off the pores leading to the interior of the particle.

Figure 20-B shows the relationship between molten slag temperature as measured by an optical pyrometer and the total and external surface areas of slag produced through a 3/32 in. diameter orifice in a 28 in. Hg vacuum. As seen, the total and external surface areas both increase with increasing temperature. It is believed that as the temperature increases, the viscosity decreases and the slag droplet becomes more fluid. Thus, dissolved gases more readily escape the fluid and cause the slag to expand; thereby, increasing the surface area.

Conclusion

Experimental results indicate that the vacuum shot tower technique is an effective means of increasing the total surface area of typical CaO-SiO_2-Al_2O_3 slags from two to five times the value for crushed slag. Based on these findings, it appears that slag granulation can serve as a means of providing increased total surface area slags for desulfurization.

SLAG DESULFURIZATION

Introduction

The slag produced in the combustor will contain between six and eight percent sulfur. By desulfurizing the slag, the problem of disposing of a high sulfur bearing material, which could be a potential source of pollution, is eliminated. Instead, part of the desulfurized slag is recycled to the combustor to take advantage of its lime content and the rest becomes a salable by-product for use in road construction. The elemental sulfur recovered from the slag is either a useful by-product or a harmlessly disposable waste (depending on sulfur market conditions). Because of the importance of desulfurization it was decided to conduct a study to determine the effect of various process parameters on reaction kinetics. Slag desulfurization was accomplished by reacting the slag with steam at elevated temperatures to produce an offgas containing elemental sulfur, H_2S and SO_2.

Experimental Procedure

The experimental program was conducted to determine the effect of slag properties and reaction variables on the kinetics of desulfurization. In particular, the effects of reaction temperature, slag external surface area, sulfur content of the slag, and concentration of water in the reaction gas on the time to achieve desulfurization and on the gaseous products of reaction were investigated.

The experimental setup is shown in Figure 21B. The reaction chamber was a 1-1/8 I.D. ceramic tube thirty inches long. Steam was carried into one end with an inert gas (N_2), contacted the slag, and exited into a series of condensers and traps designed to collect each individual species in the offgas. Steam for reaction was produced in a flask heated by a Variac-controlled mantle. At the beginning of each run the flask was charged with water and weighed. By varying the nitrogen flow rate into the flask and by adjusting the Variac both the mole fraction of steam in the gas and the throughput of steam to the reactor could be controlled. After each run the flask was stoppered, cooled, and weighed to determine the steam used.

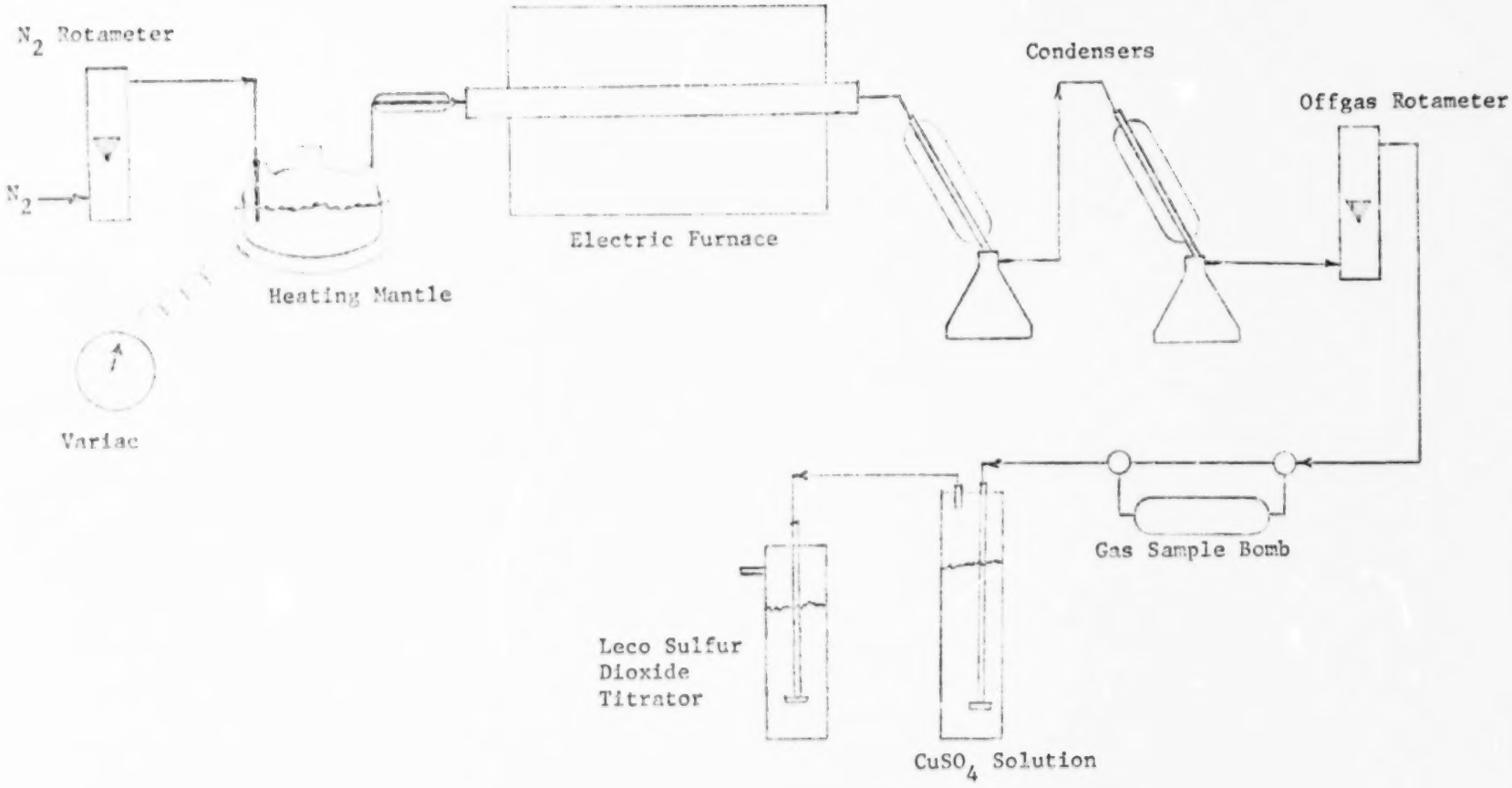


FIGURE 21B-DESULFURIZATION KINETICS EXPERIMENTAL APPARATUS

The ceramic reaction tube was charged with 40 to 60 grams of slag before it was placed in the electric resistance furnace. After a nitrogen purge of 15 minutes to remove air the ends of the tube were sealed, and the tube was placed in the furnace. After the tube reached the run temperature, its exit end was connected to the series of condensers and traps as shown in Figure 21B. The steam flask was connected to the tube entrance and with the introduction of steam and nitrogen the run was started.

As the gaseous reaction products exited the tube they were cooled by two water-cooled condensers outfitted with Erlenmeyer flasks at the bottom to trap condensing material. Elemental sulfur and unused steam condensed in these flasks. The remaining offgas (N_2, H_2S, and SO_2) passed out of the flasks, through a rotameter, and to a section of the offgas system where a bomb sample could be taken (Figure 21B).

The offgas then proceeded to a flask containing a 0.1 Molar solution of copper sulfate ($CuSO_4$). The offgas was bubbled into approximately 500 milliliters of this solution which precipitated hydrogen sulfide as copper sulfide according to the following equation:

$$H_2S + CuSO_4 \longrightarrow CuS \downarrow + H_2SO_4$$

Additionally, sulfur dioxide was absorbed in the solution due to the high solubility of SO_2 in water. Sulfur dioxide that escaped this solution passed to a Leco titrator where it was absorbed in an acid solution and was titrated with potassium iodate.

At the end of a run, the two final absorption flasks were disconnected from the system preceeding it and a flow of N_2 was introduced into the $CuSO_4$ to push some of the dissolved SO_2 into the Leco sulfur dioxide titrator. The remaining SO_2 that would not leave the $CuSO_4$ solution was determined by a direct titration of the solution with KIO_3. The reactions and theory explaining this titration for SO_2 are identical to those pertaining to the Leco sulfur dioxide titrator (explained in Appendix A under Combustor Operation). The sum of the above three titrations indicated the cumulative amount of SO_2 produced. Hydrogen sulfide was determined by titrating an aliquot of the $CuSO_4$ solution (after it has been filtered and diluted to volume) with ethylene-diaminetetraacetic acid (EDTA) to determine the concentration of cupric ion (Cu^{++}) remaining in solution. A 50-ml aliquot of the diluted $CuSO_4$ solution was withdrawn into a beaker, to which was added 10 ml of a pH 5.0 to 6.0 buffer solution, 5 drops of PAN indicator and 8 drops of xylenol orange indicator. The sample was initially pink. Upon titration with 0.020 molar EDTA solution, it turned blue and then to green. The blue to green color change was the end point of the titration. The difference between the cupric ion concentration initially in solution (i.e., the initial $CuSO_4$ concentration) and the amount at the end of the experiment indicated the amount of CuS precipitated and therefore the amount of hydrogen sulfide that passed through the solution.

To complete the experimentation, the ceramic reaction tube containing the desulfurized slag was sealed, removed from the furnace, and cooled. The slag was dumped from the tube and the total sulfur remaining in the slag was determined by the combustion-iodometric method (described in Appendix A).

Discussion of Results

Slag desulfurization is a heterogeneous reaction between water vapor in the gas phase and solid sulfur, presumably existing as calcium sulfide in the slag. Consequently, a number of rate-determining steps may be postulated. The desulfurization reaction rate may be controlled by the transfer of water vapor from the bulk gas phase to the slag particle, diffusion of reactant and products through the pores of the slag particle, or by chemical reaction kinetics. The latter is generally a strong function of temperature whereas the mass transfer steps show a much smaller dependence.

Although the reaction steps involved in the desulfurization of slag with water vapor are not known, it can be assumed that a simple stoichiometric relationship exists between the reactant and product species involved. Assuming that the reaction is controlled by the mass transfer of water vapor from the bulk gas phase to the slag, a simple material balance around a differential reactor can be written as:

$$\frac{w\ dC_s}{p\ dt} = c_1 k_g a y \qquad (1)$$

where w = weight of the slag
p = density of the slag
C_s = sulfur content of the slag
t = time
c_1 = stoichiometric conversion constant
k_g = mass transfer coefficient
a = slag specific surface
y = mole fraction of water in the gas phase

Equation (1) assumes that chemical kinetics are very rapid, and that the rate of sulfur removal from the slag particle is directly proportional to the mass transfer of water vapor from the gas phase to the slag particle. The mass transfer coefficient is a function of the flow characteristics in the reaction system and depends as well upon the physical properties of the gaseous constituents. In general*, k_g is a function of the Reynolds Number and the Schmidt Number. The Schmidt Number, a dimensionless group of variables characterizing the physical properties of the gas, remains relatively constant for small temperature

*Perry, J. H., Chemical Engineers Handbook, McGraw Hill, New York 1950, p. 547

variations. Consequently, if it is assumed that the reaction proceeds over small temperature ranges, the Schmidt number will present no significant effect on the mass transfer coefficient. With this assumption, the relationship between the mass transfer coefficient and system flow parameters given in the reference* can be expressed by the proportionality:

$$k_g \propto D^{-0.41} G^{0.59} \qquad (2)$$

where D = diameter of the slag particle
C = flow rate of the fluid

Substituting Equation (2) into one, rearranging and integrating for a constant flow system with slag particles having initial sulfur concentration C_i, the relationship:

$$1 - \frac{C}{C_i} = C_2 a G^{0.59} y t / w C_i D^{0.41}$$

where C_2 = constant defines the sulfur level in the slag as a function of reaction time.

The results of the experimental work show that the slag desulfurization reaction is essentially controlled by the mass transfer of water vapor from the bulk gas phase to the slag particle. A correlation relating the percent sulfur removed from the slag with slag physical properties and system flow characteristics is presented in Figure 22B. As can be seen, the direct proportionality between slag desulfurization and system properties is little influenced by temperature over the range of 1800-2100°F. The lack of a strong temperature effect implies that chemical reaction kinetics are fast relative to the mass transfer rate.

Perhaps the most significant variable is time at temperature. For small particle sizes, and particularly at long times (20 minutes or more), the percent desulfurization data deviate considerably to the right from the linear mass transfer relationship. This deviation exists because of the sintering effect experienced with fine slag particles at temperatures of 2000°F or more. It was observed that at slag residence times of 20 minutes or more (depending upon slag particle size), the discrete slag particles tended to fuse together and render the packed bed reactor impervious to gas flow. This was evidenced, not only by considerably increase in back pressure during experimentation, but also by difficulty in removing the packed bed from the system.

Inasmuch as the correlation of Figure 22B is based on the slag surface area characteristics prior to insertion into the reactor, the true specific surface as a function of time and temperature is unknown. Additionally, the essentially constant level of desulfurization at long residence times for the slags implies that a change in mechanism also

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*Perry, J. H., Chemical Engineers Handbook, McGraw-Hill, New York, 1950, p. 547

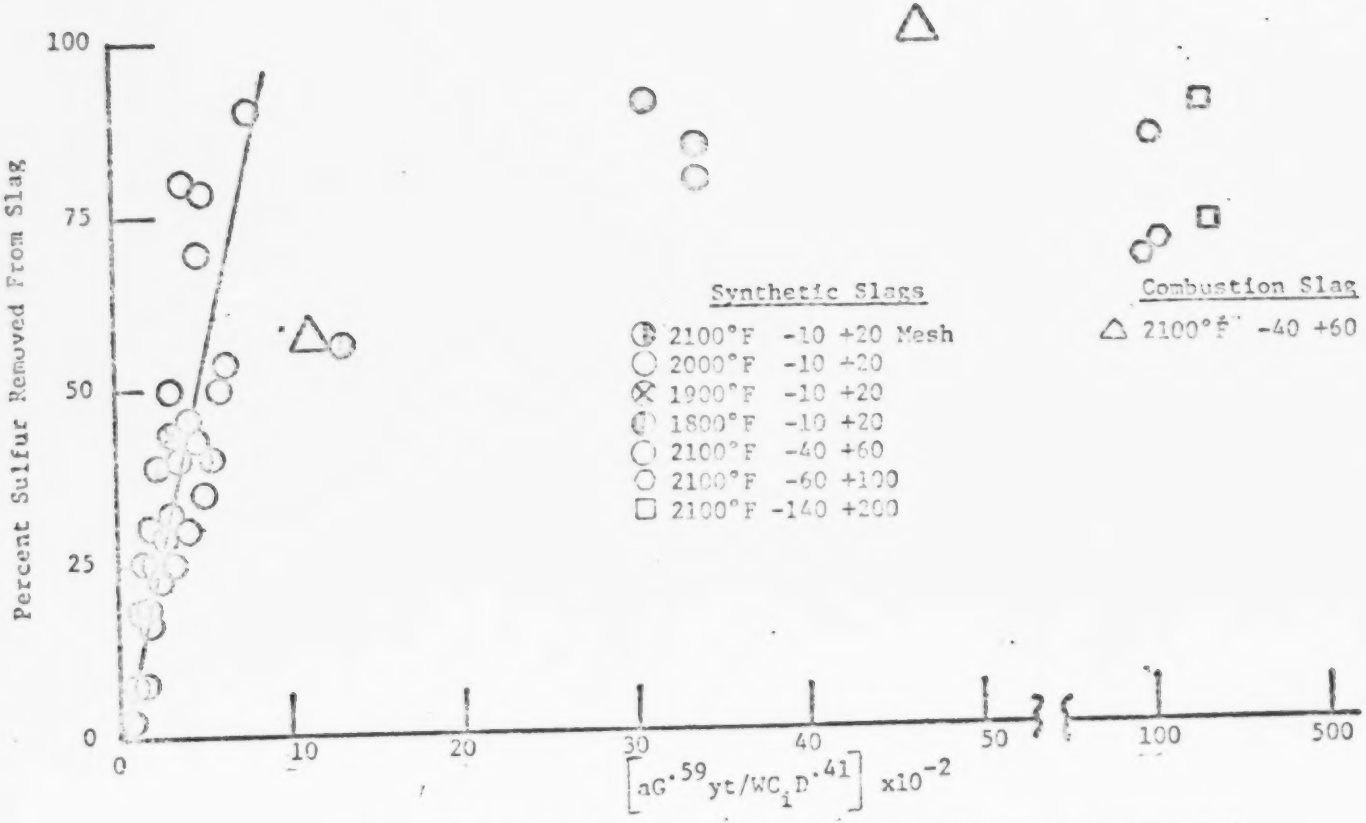

FIGURE 22B-EFFECT OF PROCESS PARAMETERS ON SLAG DESULFURIZATION

occurred. It is probably true that the sintering effect brought about a collapse or decrease in the pore size of the slag particles making them relatively impervious to the transport of reaction water to the slag interior. Speculating, it would appear that Knudsen diffusion may be the primary mechanism for bringing about desulfurization at this time.

With the exception of two points, all of the data presented in Figure 22B were obtained with synthetic slags produced in the laboratory. These slags did not contain iron oxides. On the other hand, the slags produced in the combustor contained about one percent iron oxides. Since the latter impurities could have an effect on slag desulfurization, two experiments have been completed on the desulfurization of combustor slags. These data are presented as triangles on the correlation. The results show that for a combustor slag initially containing 8.5 percent sulfur, desulfurization in excess of 99 percent can be achieved in less than two hours at 2000°F. It should be mentioned that the combustor slags did not exhibit the tendency to sinter that was exhibited by the synthetic slags.

Although the analysis of the desulfurization data (particularly with regard to correlating the offgas analysis with regard to system variables) is still continuing, typical offgas compositions as a function of desulfurization time are presented in Figure 23B. The data shown are for a coarse minus 10 plus 20 mesh slag, desulfurized at 2000°F. The offgas is a rather complicated function of water flow rate, particle size, temperature, and partial pressure of water vapor in the gas phase. The relationship between these variables is not yet understood. Nevertheless, Figure 23B is used to illustrate the general way in which hydrogen sulfide, sulfur dioxide and elemental sulfur content vary with time. In all of the experimentation conducted thus far, H_2S to SO_2 ratios have varied from a low of about 1 to a high of about 15. Elemental sulfur recovered depending upon operating conditions, varied from about 10 to 55 percent. In general, higher temperatures favor the formation of elemental sulfur and lower H_2S and SO_2 ratios. Low water input rates tend to produce high H_2S and SO_2 ratios.

The desulfurized (99 plus percent) experimental combustor slags produced an offgas whose cumulative elemental sulfur content was 53 percent and the cumulative H_2S to SO_2 ratio was 1.6 at the end of two hours.

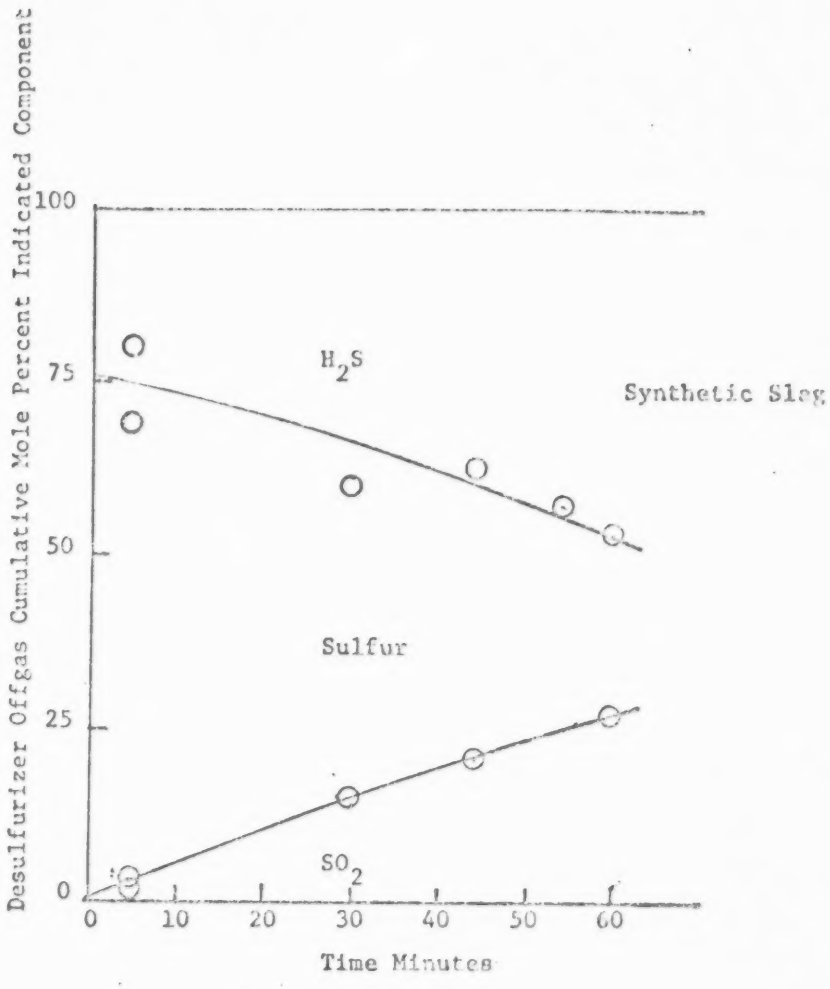

FIGURE 23D-VARIATION OF OFFGAS COMPOSITION WITH TIME AT 2000°F

APPENDIX C

PROCESS SIMULATION AND ECONOMICS

Equipment Cost

To determine the capital investment for the Two-Stage Coal Combustion Process, equipment was grouped into six main equipment complexes designated as series 1000-coal preparation, 2000-slag preparation, 3000-flux preparation, 4000-air preparation, 5000-combustor, and 6000-slag desulfurization. The cost of each item of equipment in a complex was estimated based on a size (cost) controlling process variable(s). Those items of equipment having a common size controlling variable were then combined to yield expressions of the form:

$$C = C_o S^A \qquad (1)$$

where C = estimated cost (1972)
C_o = constant
S^o = magnitude of size controlling variable, and
A = constant

which permit combined equipment costs to be estimated for any value of the size controlling variable.

The energy and material balance computer program is run to determine the capacity and/or temperature of the process streams which control the size and, consequently, the cost of the equipment. Individual equipment costs are determined using equation (1) and combined to yield the cost of an equipment complex. Process equipment cost is the sum of the costs of the individual equipment complexes.

To aid in the following discussion, the process flow diagram is presented as Figure 1C with Table IC designating the process streams shown in Figure 1C. Also a schematic layout of the process equipment designated by number appears as Figure 2C.

Coal Preparation Complex

A list of the coal preparation equipment, the design basis, and estimated cost are presented in Table IIC.

Lump coal from storage is belt conveyed (equipment number 1010-1011) into coal bucket elevator (1020) and then into a surge bin (1030) located above a coal crusher (1040-1043). The crushed coal is screened (1050-1052) and the plus 1/8 inch fraction recycled to the crusher using belt conveyor (1070-1071). Crushed coal is dried in coal dryer (1055) and belt conveyed (1060-1063) to a coal bunker (1080). A belt conveyor (1090-1092) is used to transport coal to surge bin (1100) prior to entering the pneumatic coal injection system (1110).

FIGURE - IC PROCESS FLOW DIAGRAM

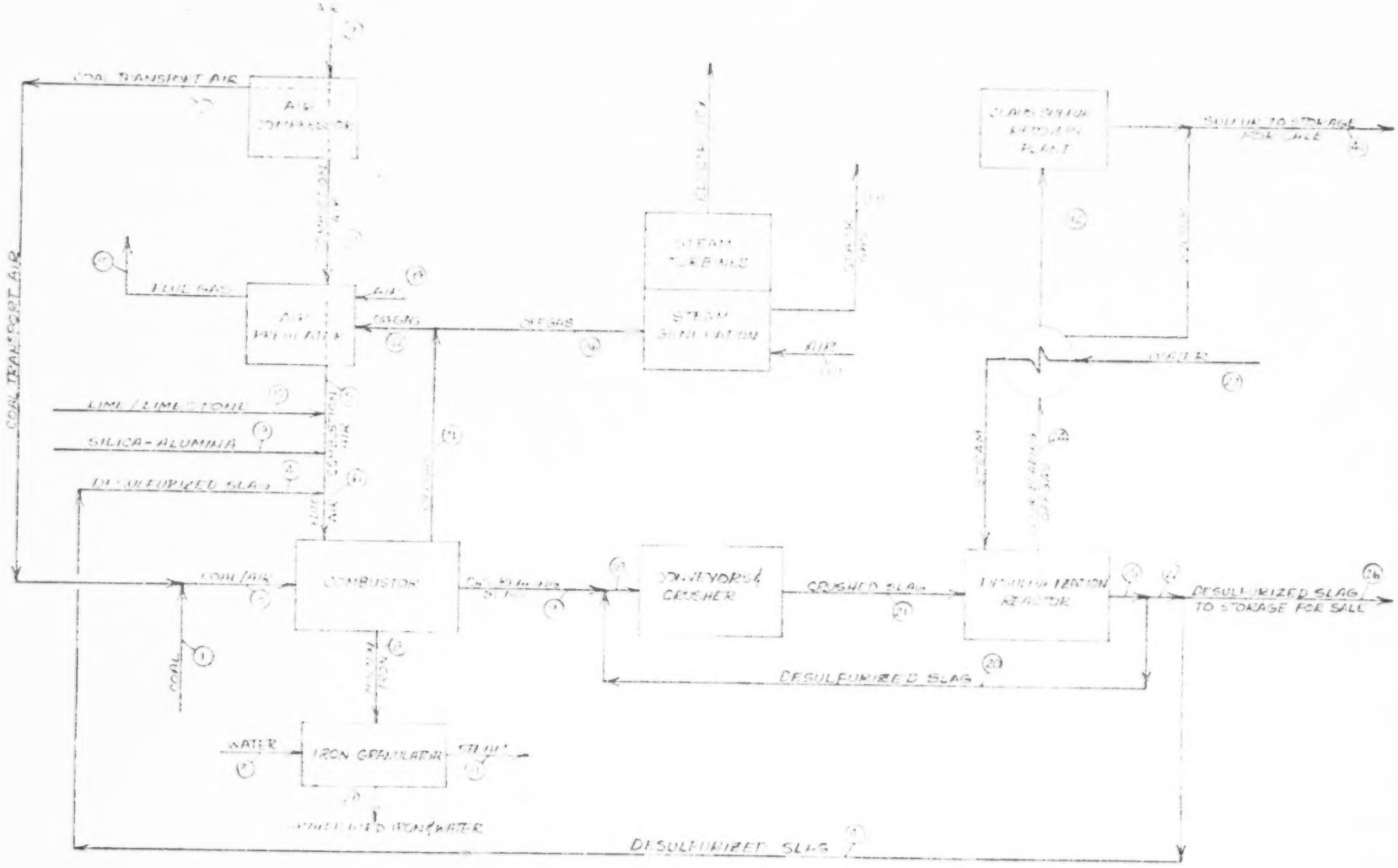

TABLE IC

PROCESS STREAM DESCRIPTION - TWO STAGE COAL COMBUSTION PROCESS

Stream	Stream Description
1	Coal
2	Coal transport air
3	Coal-air mixture to combustor
4	Desulfurized slag into combustion air stream
5	Preheated combustion air
6	Preheated air-flux mixture to combustor
7	Total air to combustor
8	Molten iron from combustor
9	CaS bearing slag to desulfurization complex
10	Lime/limestone into combustion air stream
11	Total combustor offgas
12	Air to steam generation unit
13	Stack gas from power plant
18	CaS slag to crusher
19	Silica/alumina into combustion air stream
20	Recycled desulfurized slag to cool stream 9
21	Crushed slag to desulfurization reactor
22	Desulfurized slag not recycled to stream 9
24	Desulfurization offgas
25	Desulfurized slag from desulfurization reactor
26	Desulfurized slag to storage and sale
27	Steam to desulfurization reactor
29	Granulated iron from combustor
30	Water to granulator
31	Steam from granulator
32	Combustor offgas sent to air preheater
33	Compressed combustion air
34	Air to air preheater
35	Flue gas from air preheater
36	Combustor offgas to power plant
41	Sulfur product
42	Offgas from sulfur condenser

FIGURE - 2C PROCESS EQUIPMENT LAYOUT

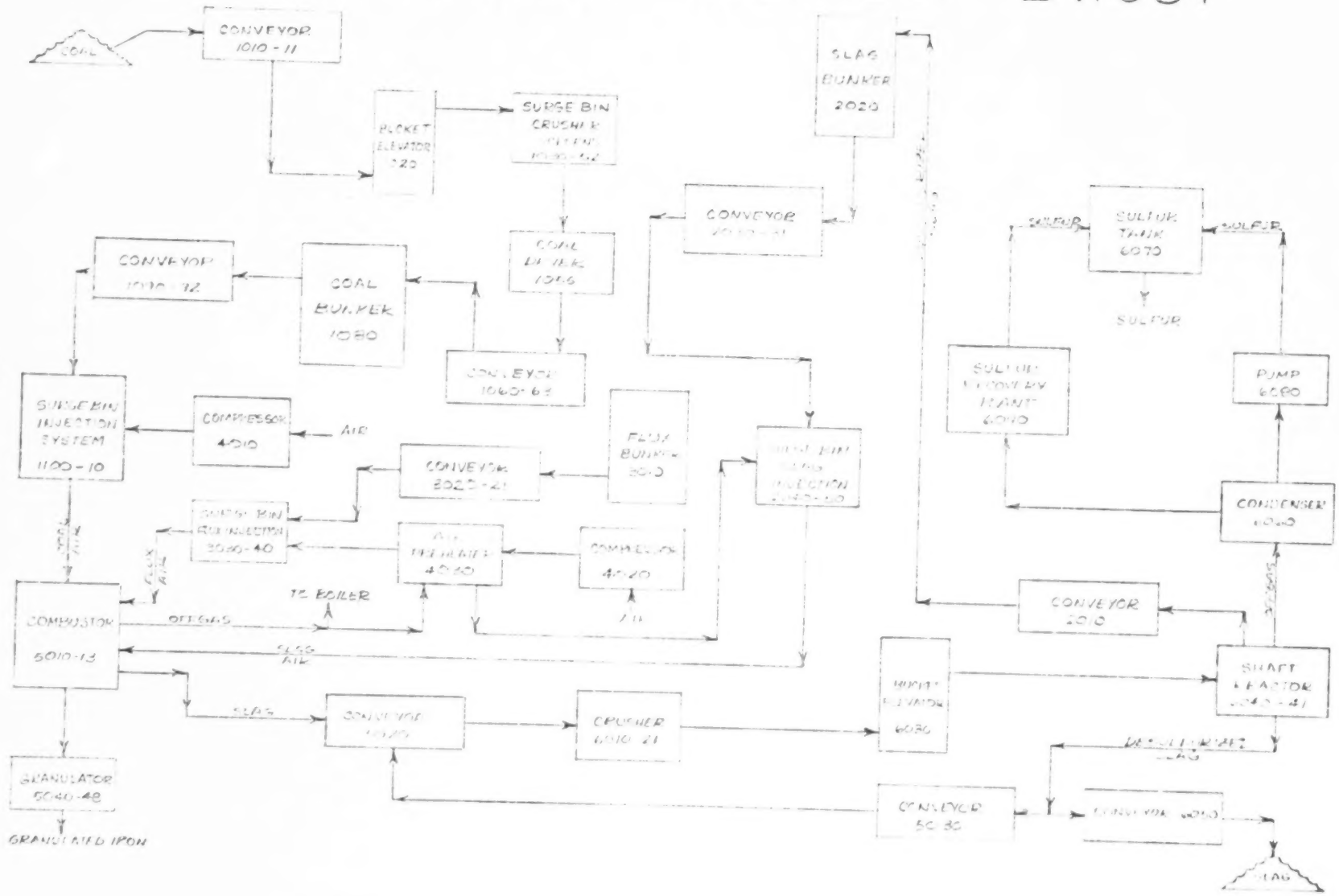

TABLE IIC

COAL PREPARATION - EQUIPMENT COSTS

Number	Equipment	Design Basis	Cost, $M
1010	Conveyor to Bucket Elevator	400 foot length, 36 inch wide belt with	37.4
1011	Motor and Drive	10 foot rise, 460 TPH coal, 15 hp motor	10.3
1020	Bucket Elevator	45 foot high, 250 TPH coal	52.0
1030	Surge Bin above Crusher	½ hour residence time, 4160 ft^3, carbon steel	15.6
1040	Coal Crusher	4 inch nominal feed, Gundlach Gage-Paktor	19.7
1041	Coal Splitter	model 50-2C 4R, 45 hp, 300 TPH coal, upper motor	1.5
1042	Motor & Drive	300 hp, lower motor 200 hp	10.3
1043	Speed Reducer		27.6
1050	Screens	6 foot x 12 foot - triple deck screens, 2 ½ hp motor,	11.6
1051	Motor and Drive	125 TPH coal	0.9
1052	Splitter		5.5
1055	Coal Dryer	No 135 Heyl Patterson Fluid Bed Dryer System 400 TPH Coal, 8% Water to 1% Water	335.0
1060	Conveyor to Coal Bunker	400 foot length, 36 inch wide belt with 50 foot	37.4
1061	Motor and Drive	elevation, 500 TPH coal, 35 hp motor	16.0
1062	Tripper		22.8
1063	Cover		9.5
1070	+1/8 inch recycle conveyor	100 foot length, 16 inch wide belt, 50 TPH	7.3
1071	Motor and Drive	coal recycle, 5 hp motor	8.8

CONTINUATION OF TABLE IIC

Number	Equipment	Design Basis	Cost, $M
1080	Bunker	12 hour storage, 350,000 ft^3 capacity ¼ inch carbon steel	363.0
1090	Conveyor to Injection System	200 foot length, 36 inch wide belt with 60 foot	49.6
1091	Motor and Drive	elevation, 460 TPH coal, 40 hp motor	20.3
1092	Cover		11.4
1100	Surge Bin-Coal Injector	½ hour storage, 1500 ft^2 capacity, 150 TPH coal	5.7
1110	Injection System	3 injection cycles per hour, 1350 ft^3 capacity 100 TPH coal	

The pneumatic injection system transports the coal into the combustor lances. The size and cost of all the equipment of a coal preparation complex is a function of the process coal rate (stream 1).

Slag Preparation Complex

A list of the slag preparation equipment, the design basis, and estimated cost are presented in Table IIIC.

Desulfurized slag from the desulfurization reactor is belt conveyed (2030) into a slag bunker (2020). Slag is belt conveyed (2030) from the bunker into a surge bin (2040) prior to entering the desulfurized slag pneumatic injection system (2050). The pneumatic injection system transports slag into the corbustor lances. An alternate method of putting slag into the combustor might be to dump the slag via a star valve located on the combustor. This, however, was considered in the combustor evaluation. All equipment was sized to handle 100 TPH of desulfurized slag; consequently, the slag preparation complex cost is a function of the recycled desulfurized slag rate to the combustor (stream 4).

Flux Preparation Complex

Flux preparation includes equipment for taking flux materials, (in most cases limestone, however, silica and alumina may also be required under certain process conditions) from a storage bunker and pneumatically injecting these fluxing agents into the combustor. A list of the flux preparation equipment, the design basis and the estimated cost are presented in Table IV-C.

Fluxing agents from a storage bunker (3010) are belt conveyed (3020) to a surge bin (3030) prior to entering the flux pneumatic injection system (3040). The flux pneumatic injection system transports the fluxing materials to the combustor lances. All equipment was sized to handle 25 TPH of fluxing materials; consequently, the flux preparation complex cost is a function of the sum of the limestone and/or lime added (stream 10), and the silica and/or alumina added (stream 19).

TABLE IVC

FLUX PREPARATION - EQUIPMENT COST

Number	Equipment	Design Basis	Cost, $M
3010	Fluxing Material Bunker	6 hour storage, 4800 ft^3 capacity, 1/2 inch carbon steel	13.0
3020	Conveyor to Surge Bin	360 foot length, 20 inch wide belt, 10 hp motor	17.1
3021	Motor & Drive		8.9
3030	Surge Bin-Flux Injector	1/4 hour residence time, 180 ft^3 capacity	5.3
3040	Flux Injection System	3 cycles per hour, 220 ft^3 capacity	58.8

TABLE IIIC

SLAG PREPARATION - EQUIPMENT COSTS

Number	Equipment	Design Basis	Cost, $M
2010	Conveyor from Desulfurization to Bunker	200 foot length, 20 inch wide belt, 10 hp motor	40.0
2020	Bunker	4 hour residence time, 12480 ft^3 capacity, ½ inch carbon steel	37.7
2030	Conveyor to Surge Bin	100 foot length, 20 inch wide belt, 7½ hp motor	9.0
2031	Motor and Drive		8.9
2040	Surge Bin-Slag Injector	½ hour residence time, 1840 ft^3 capacity	28.1
2050	Desulfurized Slag Injection	3 cycles per hour, 984 ft^3 capacity	192.0

Air Preparation Complex

The air preparation complex consists of the coal transport air compressor (4010) which compresses air (stream 2) for coal injection, the combustion air compressor (4020) which compresses air (stream 33) prior to entering the air preheater, and the air preheater (4030) which heats combustion air (stream 33) prior to entering the combustor. A list of these items is presented in Table VC where the design basis and estimated cost is given. The injection air compressor(s) is sized to yield sufficient 10 psig transport air to pneumatically inject coal into molten iron at an injection ratio of ten pounds of coal per pound of air. The estimated cost shown in Table VC for the injection air compressor is based on a 270 brake horsepower requirement. The brake horsepower requirement can be established provided the desired outlet pressure air volumetric flow rate and compressor efficiency are specified; consequently, the injection air compressor cost for any process case can be estimated by scaling the data of Table VC once the brake horsepower requirement is established. However, if the compressor efficiency and air outlet pressure are specified, then the cost is only a function of the injection air rate. (stream 2). Regardless of injection air rate a minimum of two compressors are costed.

TABLE VC

AIR PREPARATION - EQUIPMENT COSTS

Number	Equipment	Design Basis	Cost, $M
4010	Injection Air Compressor	Centrifugul steam driven turbine, 270 bhp	73.3
4020	Combustion Air Compressor	Centrifugul steam driven turbine, 0500 bhp	800.0
4030	Combustion Air Preheater	Heat exchanger with direct firing having 20000 ft^2 of heat transfer surface with the following air temperature ranges and materials	
		77-1000F, carbon steel	62.0
		1000-1200F, type 501 stainless steel	155.0
		1200-1400F, type 405/410 stainless steel	186.0
		1400-1500F, type 430 stainless steel	223.0
		1500-1600F, type 304 stainless steel	273.0
		1600-1800F, type 310 stainless steel	310.0
		1800-2100F, inconel	372.0

The combustion air compressor (4020) is sized based on total air requirement of the process, less the air required for coal injection. Combustion air is pressurized to 5 psig using centrifugal steam driven turbine compressors operating at 70 percent efficiency. As seen in Table VC, the estimated cost for a 6500 bhp compressor is $800,000. A minimum of two combustion air compressors are used; however, when the brake horsepower requirement exceeds 6500 bhp, a number of equally sized smaller compressors are costed. In the same manner, as for the injection air compressor, the estimated cost of the combustion air compressor can be made a function of only the combustion air (stream 33).

The air preheater cost will depend upon the required heat transfer surface and the materials of construction, both of which depend upon the exit temperature of the combustion air. In Table VC are shown the estimated costs for air preheaters having a 20000 square foot heat transfer surface at various exit air temperatures and the design basis. The air preheaters are assumed to be a parallel arrangement of heat exchangers each with provision for direct firing of the combustor offgas. The air preheating equipment cost is determined using an overall heat transfer coefficient of 5 BTU/ft^2-hr-°F to establish the required heat transfer surface to raise combustion air (stream 33) from 77°F to the desired exit temperature. Since the exit air temperature is known, the cost for a 20000 ft^2 air preheater can be determined from Table VC. The air preheaters are limited to a maximum size of 20000 ft^2; consequently, several equally sized units are costed depending on the total heat transfer surface requirement.

Combustor Complex

The combustor complex consists of a combustor with lances, enclosed conveyors which remove liquid combustor slag, enclosed conveyors which combine this hot slag with cooler slag for belt protection, and an iron granulation system. The depth of molten iron in the combustor is established by the required immersion lance depth to fully dissolve the coal. Experimentation has shown that a 24 inch immersion depth will suffice; consequently, the combustor is conservatively assumed to contain a 3.5 foot molten iron bath. The area of the combustor is controlled by either of two design criterias. There must be a sufficient weight of iron in the combustor to accommodate the dissolving coal such that a solution rate of .25 weight percent carbon/minute is not exceeded. That is, the combustor area (or the weight of iron since the height is fixed) must be sufficiently large to dissolve the coal. In addition, there must be sufficient combustor area to prevent the offgas velocity from the bath surface from being excessive with subsequent carryover of dust. Based on steelmaking basic oxygen furnace technology, the superficial offgas velocity was limited to 30 ft/sec. In general, when air was used to burn from the molten iron, the superficial offgas velocity criteria (30 ft/sec) controls the combustor area (weight of metal in the combustor). When oxygen is used to burn metal carbon, the solubility rate will determine the bath weight. The volumetric flowrate of the offgas will depend on a number of factors such as the combustor pressure and temperature, and coal composition and the quantity of air needed.

In order to facilitate estimating the cost of various sized combustors, the 48 foot I.D. combustor as depicted in Figure 3C was used. As seen, the combustor is a steel shelled refractory lined vessel with a 2 1/2 foot refractory lining at the base and sides. In Table VIC is shown costs for the combustor shell (5010), refractory lining (5011), lances (5012), and lance cooling pumps (5013). Twenty five lances and pumps were assumed to be required. The combustor shown in Figure 3C will contain 1200 tons of iron. The required weight of iron as determined by either the coal solubility rate or offgas superficial velocity criteria was used to scale the combustor costs of Table VIC. The number of combustors to use in a given power plant application is assumed to be three equally sized units--any two of which can supply the full energy requirements of the plant.

The iron granulation system includes the equipment designated as 5040 to 5048 in Table VIC. The cost of this system is based on the quantity of molten iron contained in a single combustor and not by the iron production rate from the iron contained in the coal. That is, the iron granulation system is sized to remove all the iron from a combustor in a specified time. To establish the cost of the iron granulation system, the total combustor iron is divided by the specified removal time to obtain an iron removal rate and the costs of Table VIC scaled accordingly.

The combustor complex includes enclosed belt conveyors for removal of slag from the combustor and belt conveyors used to place a cool layer of desulfurized slag on the above conveyors. These are designated as slag pan conveyor (5020) and slag recycle apron conveyor (5030). The estimated costs shown are based on 120 TPH slag removal rate from the combustor and 20 TPH desulfurized slag recycle rate to the pan conveyor. The cost of the pan conveyor is scaled based on the CaS bearing slag leaving the combustor (stream 9). The cost of the recycle apron conveyor is based on recycled desulfurized slag (stream 20).

Slag Desulfurization

The slag desulfurization complexes receives CaS bearing slag from the slag pan conveyor (5020-combustor complex) and crushes it in a primary roll type crusher and a secondary crusher (6010-6021). A bucket elevator (6030) is used to convey the crushed slag into a refractory lined shaft reactor (6040-6041). The sulfur bearing offgas from the shaft reactor proceeds to sulfur condenser (6060) where the sulfur is condensed out and pumped (6080) to a sulfur collection tank (6070). The remaining H_2S-SO_2 offgas is sent to a Claus sulfur recovery plant (6090) where sulfur is produced and sent to the sulfur collection tank (6070). The desulfurized slag leaving the shaft reactor is split into three streams, respectively, to the slag bunker via a conveyor (2050-slag preparation), recycled back to the slag pan conveyor via the slag recycle apron conveyor (5030-combustor) and sent to pile storage using conveyor (6050). In Table VIIC, the equipment comprising the desulfurization complex, the design basis, and estimated cost are presented. For cost estimating

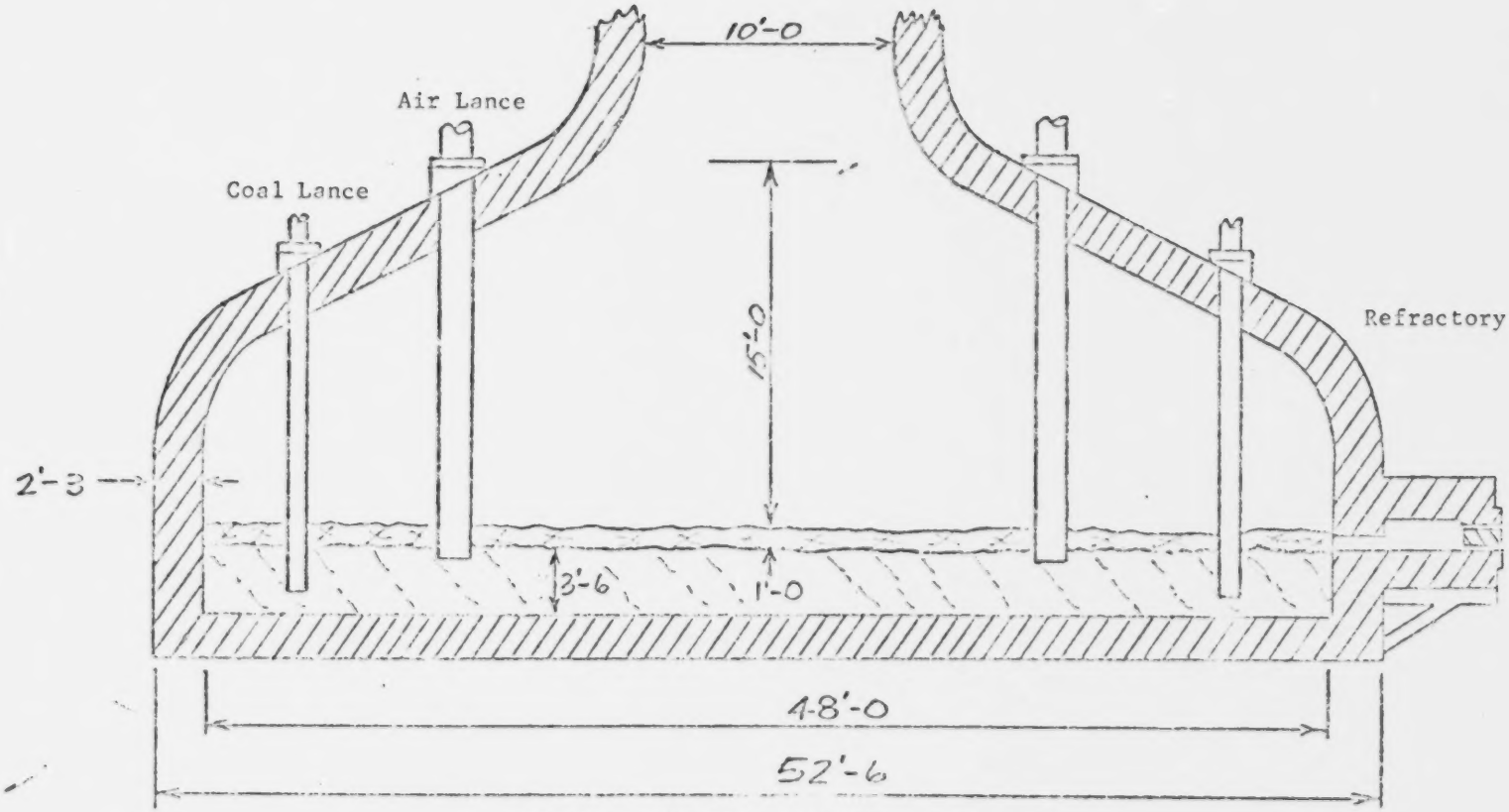

FIGURE 3C-48 FOOT DIAMETER COMBUSTOR

TABLE VIC

COMBUSTOR - EQUIPMENT COSTS

Number	Equipment	Design Basis	Cost, $M
	Combustor		
5010	shell	48 foot I.D. combustor as shown in Figure 3C	308.0
5011	refractory	40 psig, carbon steel, containing 1200 tons	168.0
5012	lances	iron high density alumina brick, 25 lances and	80.0
5013	lance cooling pumps	pumps	7.0
5020	Slag Pan Conveyor	Link belt conveyor, 70 foot length, 120 TPH 15 hp motor	60.0
5030	Slag Recycle Apron Conveyor	100 foot length, 50 TPH, 7½ hp motor	20.0
	Iron Granulation System		
5040	tundish	10 feet L x 6 feet W x 6 feet D, 1.5 feet thick brick	4.3
5041	runner	4 - 15 feet long	2.4
5042	water sprays	20 inch spray plate with ¼ to ½ inch holes	.1
5043	tank	54 foot x 22 foot x 20 foot deep tank	68.7
5044	hopper guide	20 foot x 12 foot guide	1.5
5045	discharge bell	110 foot long, 36 inch wide rubber belt with variable drive, 15 hp	27.7
5046	cooling and settling tank	26 foot x 22 foot x 20 foot deep tank	25.6
5047	granulator pump	13000 GPM, 15 psig, 150 hp	14.2
5048	granulated iron conveyor	110 foot long, 36 inch wide rubber belt with variable drive, 15 hp	27.7

TABLE VIIC

DESULFURIZATION - EQUIPMENT COSTS

Number	Equipment	Design Basis	Purchase Cost
6010	Primary Crusher	Gunlach model 45 DACC, heavy duty Two-Stage Four Roll Crusher, 75 hp, 220 TPH capacity	42.0
6020	Secondary Crusher	Gunlach model 50-2C4R Cage Packer, 220 TPH capacity	30.6
6021	Speed Reducer		25.0
6030	Bucket Elevator	50 foot height, 100 hp motor, 220 TPH capacity	28.0
6040	Desulfurizing Shaft Reactor	½ hour residence, 60% loading, 5000 ft^3	50.0
6041	Refractory	alumina refractory	12.0
6050	Conveyor for Slag to Storage	100 foot length, 14 inch wide belt	20.0
6060	Sulfur Condenser	Heat load 6.3 MM BTU/hr, 6000 ft^2 heat transfer surface, stainless steel, 14 TPH sulfur	50.0
6070	Sulfur Collection Tank	24 hour storage, 336 tons sulfur, 11200 ft^3	33.6
6080	Pump	3500 GPM, 45 hp motor, 15 psig	11.2
6090	BS&B Sulfur Recovery Plant	Black, Sivalls & Bryson installed plant to produce 6 TPH of Sulfur	270.0

purposes, the equipment designated as 6010-6041 is a function of the CaS bearing slag entering the shaft reactor (stream 18). The sulfur condensing, pumping, and collection system is a function of the total sulfur condensed from the offgas which, based on laboratory experimentation, was set at one half of the total sulfur produced in the process (stream 41). The cost of the Claus sulfur recovery plant is based on recovery of the remaining sulfur. The cost for the Claus sulfur recovery plant is from internal sources.

Cost Controlling Variables

In Table VIIIC is presented a summary of the process equipment grouped according to the cost controlling variables which are used to scale the costs shown in Tables IIC - VIIC. As seen, most of the cost controlling variables are the rates (TPH) for the various process streams. In the case of the injection and combustion air compressors, as previously explained, additional simplification in cost estimating is possible if the outlet pressures are specified. With the outlet pressures specified at 10 psig for the injection air and 5 psig for the combustion air, the cost of these items are proportional to streams 2 and 33, respectively. If the external heat transfer coefficient and the outlet air temperature is specified for the air preheater then the heat transfer area, or in essence, the air preheater cost is proportional to the quantity of air to be preheated (stream 33). The quantity of iron in the combustor(s) which determines cost is calculated using as a design criteria, the offgas velocity. If the combustor offgas rate (stream 11), composition pressure and temperature are known then the volumetric offgas flow rate can be established. Using 30 ft/sec as the desired offgas velocity, the required surface area of the combustor can be determined. This area is then divided by two to establish the area of each combustor for a two-combustor operation. Since a 3.5 foot high bath of molten iron is required for total coal solubility, the known volume of weight contained in each combustor is established. The cost of a combustor is, therefore, related to its iron content. To insure totally reliability, three instead of two combusors are costed--each capable of supplying 50 percent of the offgas requirement for a power plant boiler. The iron granulator is sized to empty the contents of a single combustor in eight hours.

In Table IXC are presented the factors C_o and A to be used in equation (1) to determine the cost of the various items of equipment. Also shown is the cost controlling variable S. These factors (C_o and A) were determined using the cost data of Tables IIC - VIIC, by combining the equipment associated with each cost controlling parameter and determining the combined cost over a range of values for the cost controlling variable. Plotting the resulting cost versus the cost controlling variable enabled values for C_o and A to be determined.

Total Purchased Equipment Cost

To establish the total purchased equipment cost, the energy and material balance computer program was run to ascertain process stream rates. For a 1000 MW power plant using coal of the composition shown in Table XC, the process stream rates of Table XIC were determined.

TABLE VIIIC

COST CONTROLLING VARIABLES

Equipment

Complex	Number(s)	Cost Controlling Variables
Coal Preparation	1010 - 1110	Coal rate to combustor, stream 1
Slag Preparation	2010 - 2050	Recycled desulfurized slag rate to combustor, stream 4
Flux Preparation	3010 - 3040	Flux rate to combustor, stream 10 plus 19
Air Preparation	4010	Brake horsepower requirements to compress injection air, stream 2
Air Preparation	4020	Brake horsepower requirement to compress combustion air, stream 5
Air Preparation	4030	Heat transfer surface required to heat combustion air to temperature, stream 5
Combustor	5010 - 5013	Combustor iron requirement based on offgas velocity criteria, stream 11
Combustor	5020	CaS bearing slag to shaft reactor, stream 18
Combustor	5030	Desulfurized slag recycled to conveyor, stream 20
Combustor	5040 - 5048	TPH iron removal rate which is function of the weight of iron in combustor
Desulfurization	6010 - 6041	CaS bearing slag to shaft reactor, stream 18
Desulfurization	6050	Desulfurized slag to storage, stream 26
Desulfurization	6060 - 6080	Fraction of total sulfur produced in process stream 41 which is condensed out prior to sulfur recovery plant
Desulfurization	6090	Fraction of total sulfur produced in process stream 41 which is formed in sulfur recovery plant

TABLE IXC

EQUIPMENT COST FACTORS

Equipment		C	A	S
Coal Preparation	1010-1110	17,080	.809	Stream 1
Slag Preparation	2010-2-5-	19,348	.696	Stream 4
Flux Preparation	3010-3040	14,958	.603	Stream 10 plus 19
Air Preparation	4010	6,220	.883	Stream 2_1^1
	4020	2,060	.941	Stream 5_2^1
	4030	302	.989	Stream 5_2^2 (0-1000F)
		817	.979	Stream 5_2^2 (1000F-1200F)
		956	.983	Stream 5_2^2 (1200F-1400F)
		1,110	.989	Stream 5_2^2 (1400F-1500F)
		1,320	.991	Stream 5_2^2 (1500F-1600F)
		1,454	.996	Stream 5_2^2 (1600F-1800F)
		1,812	.992	Stream 5^2 (1800F-2100F)
Combustor	5010-5013	8,834	.600	Tons iron in each of three combustors
	5020	2,655	.652	Stream 18
	5030	1,605	.647	Stream 20
	5040-5048	5,294	.612	Iron Granulation Rate
Desulfurization	6010-6041	3,549	.735	Stream 18
	6050	1,584	.647	Stream 26
	6060-6080	18,983	.608	50% of Stream 41
	6090	91,900	.600	50% of Stream 41

1 Assumes injection air will be compressed to 10 psig and combustion air to 5 psig.

2 Assumes an overall heat transfer coefficient of 5 BTU/hr-ft^2 F and air leaving at maximum temperature in range specified.

Using the process stream rates of Table XIC, the values of C and A from Table IXC and equation (1) enable the costs for each individual equipment complex to be determined. For the process case under consideration, the total purchased equipment cost is shown in Table XIIC, where the cost is seen to be $7.04 MM.

TABLE XC

COAL COMPOSITION

Ultimate Analysis	Med Ash
Total Carbon	68.1%
Hydrogen	5.0
Oxygen	7.3
Nitrogen	1.5
Sulfur	3.6
Ash	14.5
Higher Heating Value, 1% Moisture, BTU/lb	12500

TABLE XIC

PROCESS STREAM RATES - 1000 MW POWER PLANT

Stream	Ton/Hr	Temp-F
1	361.	108.
2	36.	100.
3	397.	108.
4	103.	1501.
5	1186.	1182.
6	1312.	1189.
7	1222.	77.
8	6.	2500.
9	166.	2500.
10	24.	77.
11	1536.	2500.
12	2177.	77.
13	3595.	304.
18	333.	2000.
20	167.	1501.
21	327.	1800.
22	153.	1501.
24	107.	1501.
25	320.	1501.
26	50.	77.
27	72.	77.
29	10.	151.
30	6.	77.
31	3.	212.
32	117.	2500.
33	1186.	77.
34	188.	77.
35	306.	399.
37	1418.	2500.
41	13.	832.
42	94.	832.

TABLE XIIC

TOTAL PURCHASED EQUIPMENT COST

Equipment	S^4 (TPH)	Cost, $M	
1010 - 1110		1.830	
1. Coal Preparation	361		1.83
2010 - 2050	103	0.320	
2. Slag Preparation			.32
3010 - 3040	24	0.100	
3. Flux Preparation			.10
4010	36	0.030	
4020	1186[1]	1.600	
4030	1186[1]	0.850	
4. Air Preparation			2.48
5010 - 5013	850[2]	1.500	
5020	333	0.118	
5030	167	0.004	
5040 - 5048	106[3]	0.091	
5. Combustor			1.71
6010 - 6041	167	.260	
6050	50	.020	
6060 - 6080	6.5	.059	
6090	6.5	.261	
6. Desulfurization			.60
TOTAL PURCHASED EQUIPMENT COST			7.04

1. For an air preheater in 1000-1200°F cost range.
2. 850 tons of iron in each of three 38 foot diameter combustors. Calculation presented in discussion section of report.
3. Iron granulation rate = 850 tons/8 hour = 106 TPH.
4. Magnitude of size controlling variable, equation (1)

Estimated Fixed Capital Requirements

Once the total purchased equipment cost is known, the total fixed capital requirement for the Two-Stage Coal Combustion Process can be calculated as shown in Table XVIIC. The application of factors for installation, etc., engineering, and construction are commonly used in engineering estimates. A contingency of ten percent, contractor's fee of six percent, escalation to 1980 and interest during construction are included to yield the total fixed capital requirement. As seen, the total fixed capital is $23.1 MM and represents the retrofitting cost for installing the process into an existing facility.

Power Plant Costs

In order to estimate the fixed capital requirement for a grass roots 1000 MW Two-Stage Coal Combustion Power station, fixed power plant capital costs were obtained. These costs are shown in Table XIVC for coal-fired and gas-fired boiler operations producing 3500 psig - 1000°F steam. Costs are shown using the standard TVA costing procedure and include escalation to 1980 and interest during construction. As seen, the total fixed capital requirement for the coal and gas-fired plants are $163. 0M and $139.3 M, respectively, and differ because of boiler plant equipment costs and an oil burning standby facility included in the gas-fired plant. The Two-Stage Coal Combustion Process produces an effluent for use in a power plant boiler; consequently, in any grass roots installation, it is probable that power plant costs can be approximated using the costs of a gas-fired facility. Therefore, to establish the cost of a Two-Stage Coal Combustion Power Station, the capital cost of Table XVIIC ($23.1 MM) was combined with the gas fired fixed capital requirement to yield a total cost of $162.8 MM. This is shown in Table XIVC. The results of Table XIVC permit a comparison to be made between a conventional coal burning facility and a Two-Stage Coal Combustion Process--gas fired facility; as seen, the fixed capital requirements are $163.2 MM and $162.8 MM respectively.

The coal fired plant has a net output of 1012 MW whereas the ATC gas fired facility produces 1000 MW. The capital cost per kilowatt are then 161.3 $/KW for the coal fired facility and 162.8 $/KW for the Two-Stage Coal Combustion power station. Thus, an additional capital requirement of $1.5/KW yields a non-$SO_2$ polluting power station.

Operating Costs

Operating costs for the coal fired power plant and the Two-Stage Coal Combustion power station are compared in Table XVC for a 70 percent

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1, "Technical and Economic Feasibility of Advanced Power Cycle and Methods of Producing Non-Polluting Fuels for Utility Power Stations", NAPCA, Contract CPA 22-69-114, 1970.

TABLE XIIIC

ESTIMATED FIXED CAPITAL REQUIREMENT
TWO STAGE COAL COMBUSTION PROCESS
1000 MW POWER PLANT

	EQUIPMENT COMPLEX	$MM
	Coal Preparation	1.83
	Slag Preparation	0.32
	Flux Preparation	0.10
	Air Preparation	2.59
	Combustor	1.71
	Desulfurization	0.60
1.	Total Purchased Equipment Cost	7.15
	Installation, Piping, Electrical Instrumentation, Utilities (70% of 1)	5.00
2.	Physical Plant Costs	12.15
	Engineering and Construction (30% of 2)	3.63
3.	Direct Plant Cost	15.78
	Contingency (10% of 3)	1.58
	Contractor's Fee (5% of 3)	.79
4.	T O T A L	18.15
	Escalation to 1980 (14.75% of 4)	2.67
5.	T O T A L	20.82
	Interest During Construction (12.0% of 5)	2.51
6.	T O T A L F I X E D C A P I T A L (1980)	23.33

TABLE XIVC
ESTIMATED CAPITAL REQUIREMENTS
For 1000 MW Power Plant Systems
All Figures in $ Thousand

	Conventional* Coal Burning	Gas-Fired Boiler* With Combustor
Land and Rights	30	30
Structure and Improvements	9,107	7,582
Boiler Plant Equipment	55,492	39,200
Turbine-Generators	34,612	34,612
Electrical Equipment	10,138	10,138
Misc. Power Plant Equipment	463	463
Station Equipment	1,572	1,572
1. TOTAL	111,414	93,597
Other Expense (12.5% of 1)	1,393	1,250
2. TOTAL	112,807	94,847
Eng.-Design-Const.-Super., Contingency (12% of 2)	13,537	12,436
3. TOTAL	126,344	107,283
Escalation (1980) (14.75% of 3)	18,636	15,824
4. TOTAL	144,980	123,107
Interest During Construction (12.6% of 4)	18,267	15,511
5. TOTAL	163,247	138,618
Standby Oil Facility	0	1,725
6. TOTAL	163,247	139,485
Two-Stage Coal Combustion Plant Cost	0	23,334
7. TOTAL	163,247	162,819
Net MW Output	1,012	1,000
Capital Cost $/KW	161.3	162.8

*All cost and factors except coal combustion process cost from "Technical and Economic Feasibility of Advanced Power Cycle and Methods of Producing Non-Polluting Fuels for Utility Power Stations", NAPCA, Contract CPA 22-69-114, 1970.

load factor operation. A capital interest charge of 14 percent, operation, supplies, and maintenance costs at 2 percent of the fixed capital requirement, and coal at $0.30/MMBTU were assumed. As shown, the operating cost is 6.57 mills per kilowatt hour for the coal fired facility and 6.82 mills per kilowatt-hour for the Two-Stage Coal Combustion power station. Thus, the Two-Stage Coal Combustion power station has a slightly higher operating cost (.25 mills per kilowatt-hour) than the coal burning - SO_2 polluting power station. When credits for iron ($20/ton), slag ($0.5/ton), and sulfur ($20/ton) are taken, the Two-Stage Coal Combustion power station operating cost is reduced to 6.40 mills per kilowatt-hour.

Power Plant Operating Costs and Process Parameters

Incorporated into the energy and material balance computer program are sub-programs which allow the fixed capital requirement and operating cost to be estimated as a function of various process parameters. That is, the economic effect of process variables such as coal composition, moisture in the coal, combustor temperature, flux composition, combustor slag basicity and the percent sulfur in the combustor slag can be established. In this manner, optimum economic ranges for these important process parameters can be determined.

TABLE XVC

ESTIMATED OPERATING COST
1000 MW Power Plants

All Figures in Mills per Kilowatt-Hour

	Conventional Coal Burning	Natural-Gas-Coal Combustion Process
Capital Charge (14% Rate)	3.683	3.717
Operating, Supplies & Maintenance	0.323	0.326
Coal ($0.3/MM BTU)	2.567	2.710
Limestone ($3/Ton)	0	0.068
Iron Credit ($20/Ton)	0	(0.129)
Slag Credit ($0.5/Ton)	0	(0.025)
Sulfur Credit ($20/Ton)	0	(0.263)
TOTAL POWER COST Mills per Kilowatt Hour	6.572	6.403
TOTAL POWER COST Without By-Product Credits	6.572	6.820

Table XVIC shows the effect of coal composition on a number of process variables and on operating cost. Three coals were used and classified as high, medium, and low ash. The important conclusions from Table XVIC are:

1. The required air preheat temperature is in the narrow range of 1000-1200°F for the wide range of coal used.

2. The capital requirement for the Two-Stage Coal Combustion Process plant is essentially independent of coal composition and is about $23/KW.

3. The net capital cost increase of a Two-Stage Coal Combustion Process - power station over a conventional coal burning facility is essentially independent of coal composition and equal to approximately $1.5/KW.

4. The operating cost ranges from a high of 6.73 mills/KW hr for the high ash coal to a low of 6.40 mills/KW hr for the medium ash coal.

In Figure 4C is shown the air preheat temperature and operating cost (mills/KW-hr with by-product credit) as a function of combustor operating temperature for a process using the medium ash coal of Table XVIC. As seen, both the air preheat temperature and operating cost increase as the combustor temperature increases. Consequently, the combustor should be operated at as low a temperature as possible consistent with maintaining a fluid slag. The suggested combustor operating temperature range is indicated and the operating cost for conventional coal burning plant is shown for comparison in Figure 4C. In the expected combustor operating temperature range the air preheat temperature will be between 1000 to 1200°F.

The moisture content of the coal is an important economic consideration because the decomposition of water to hydrogen and oxygen in the combustor is highly endothermic. In Figure 5C is shown the effect of the moisture content of coal on both the air preheat temperature and the operating cost. As seen, both the air preheat temperature and operating cost increase as the coal moisture increases. This is expected since increased quantities of coal are required to overcome the endothermic decomposition of water. Based on this result, the input coal moisture should be reduced to as low a value as practical. The suggested coal moisture range for coal entering the process is shown in the figure and should be about 1-1 1/2 percent.

TABLE XVIC

EFFECT OF COAL COMPOSITION ON OPERATING & ECONOMIC DATA*
(1000 MW Power Plant)

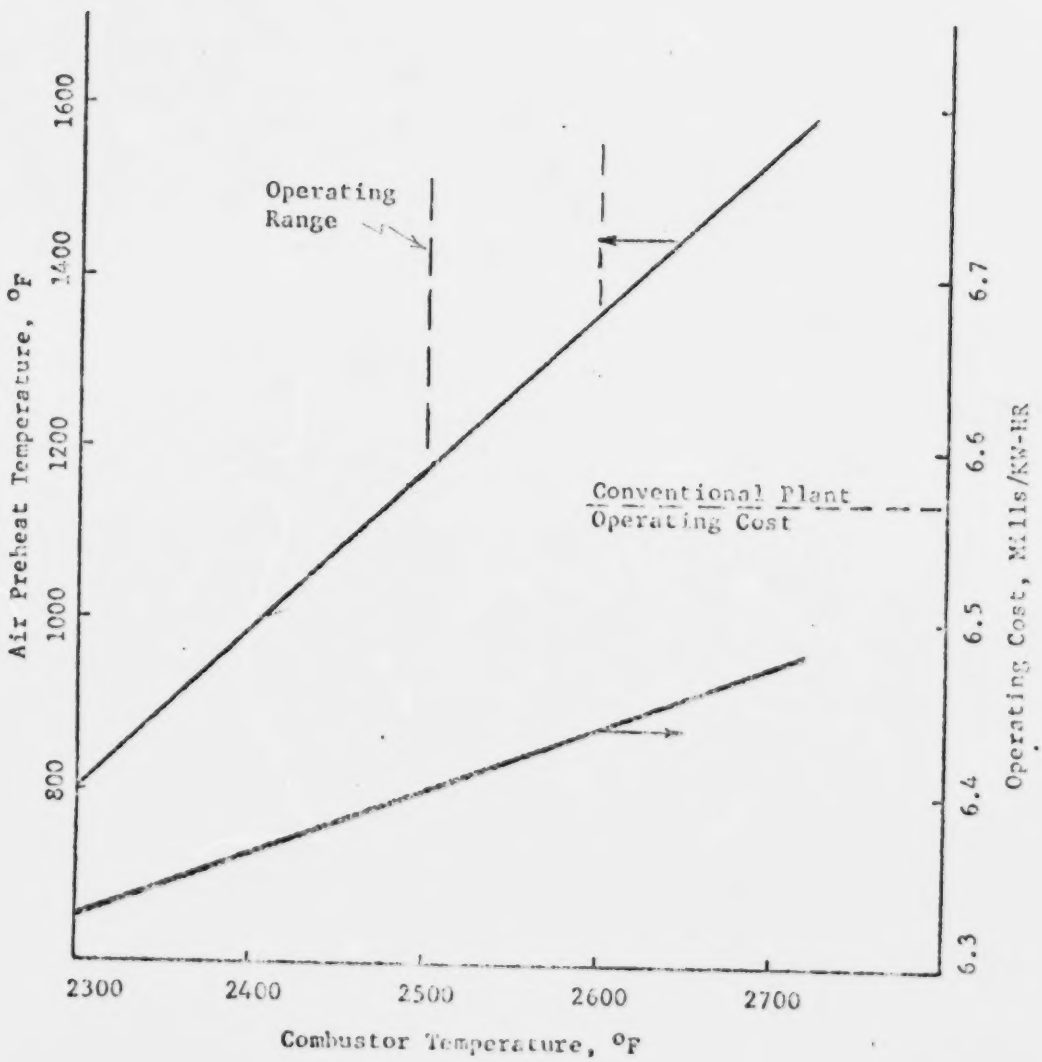
Coal (Ultimate Analysis)	High Ash	Med Ash	Low Ash
Total Carbon	62.6%	68.1%	74.6%
Hydrogen	5.0	5.0	5.0
Oxygen	7.3	7.3	7.3
Nitrogen	1.5	1.5	1.5
Sulfur	3.6	3.6	3.6
Ash	20.0	14.5	8.0
Higher Heating Value, 1% Moisture, BTU/lb**	11700	12500	13500
Air Preheat Temperature, F	1200	1182	1015
Coal, TPH	390	361	350
Limestone, TPH	9	24	12
Lime, TPH	16	0	0
Sulfur Bearing Slag to Desulfurization, TPH	178	166	159
Combustor Offgas to Steam Generation, TPH	1395	1418	1443
Combustor Air, TPH	1202	1222	1240
Sulfur Produced, TPH	14	13	13
Iron Produced, TPH	7	6	6
Slag Produced, TPH	100	60	30
Coal Combustion Process Plant Cost, $MM	23.49	23.33	23.16
Power Plant Cost, Gas-Fired Boiler Plus Combustor $/KW	162.98	162.82	162.65
Power Plant Cost, Coal Fired Boiler, $/KW	161.31	161.31	161.31
Net Increase in Power Plant Cost, $/KW	1.67	1.51	1.34
Cost of Coal at $0.30/MMBTU, $/Ton	7.02	7.50	8.11
Operating Cost, Conventional Coal Burning Boiler, Mills/KW-HR	6.57	6.57	6.57
Operating Cost - Mills/KW-HR ($0.30/MMBTU Coal)			
With By-Product Credit	6.73	6.40	6.48
Without By-Product Credit	7.19	6.82	6.87

*2500°F Combustor Temperature, 0.1 Slag Basicity, 8% Sulfur Slag

**Dulong's Equation

FIGURE 4C

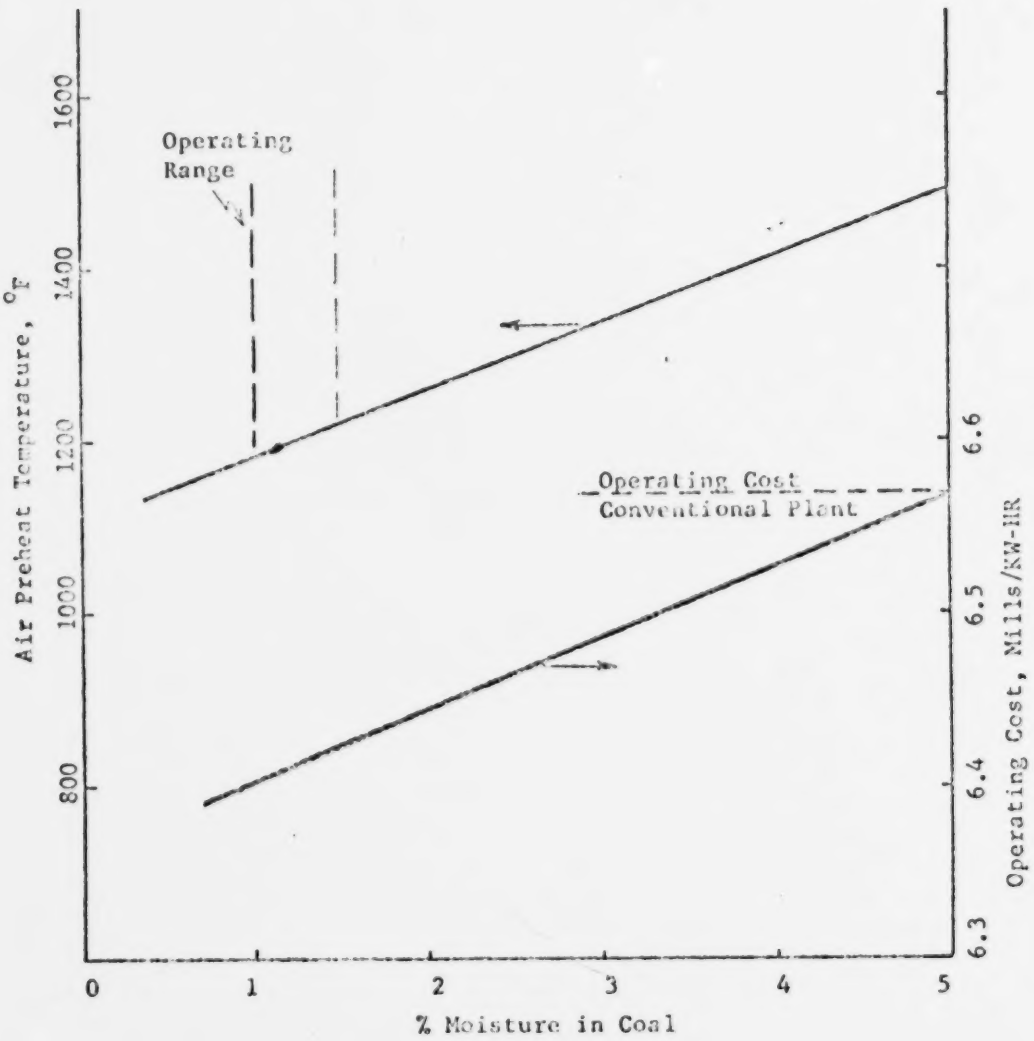
OPERATING COST/AIR PREHEAT TEMPERATURE
VS COMBUSTOR TEMPERATURE*



* 14.5% Ash - 1% Moisture Coal
.1 Basicity Slag, 8% Slag, Limestone

FIGURE 5C

OPERATING COST/AIR PREHEAT TEMPERATURE
VS % MOISTURE IN COAL*



* 14.5% Ash Coal, 2500°F Combustor Temperature,
.1 Basicity Slag, 8% Sulfur Slag, Limestone

A choice exists whether to use lime, limestone, or combination of the two as coal ash fluxing materials. In some instances, lime may be preferred (despite its high cost) because it yields a combustor operation with a lower air preheat temperature requirement. This results because the endothermic calcination of limestone to lime in the combustor is eliminated if lime is used. In Figure 6C is shown the effect of the fraction of limestone in the flux on operating cost and air preheat temperatures. As seen, the limestone fraction has a significant effect on operating cost. For example, below about 50 percent limestone in the flux, the process has a higher operating cost than the conventional plant, whereas above 50 percent limestone, the operating cost is lower. Consequently, a minimum of lime (preferably none) should be used in the process consistent with maintaining a reasonable air preheat temperature. For extremely high ash or low grade coals, lime may be required to reduce the air preheat temperature (or in essence, air preheater capital costs) and can also serve as a combustor temperature controlling variable when process coal composition varies widely during operation.

Slag basicity is an important economic consideration because basicity is related to limestone consumption in the process. Figure 7C shows the effect of slag basicity on both the air preheat temperature and operating cost. As seen, the air preheat temperature increases from about 1200°F at a basicity of 0.1 to about 1500°F at a basicity of 0.8. Also the operating cost increases quite substantially in the 0.1 to 0.8 basicity range. Operating costs are affected by basicity in two important ways. The process limestone requirement or the limestone cost per kilowatt hour increases proportionately with basicity. And desulfurization capital increases because more slag handling and larger sized equipment is required. To yield a minimum operating cost as low a basicity as possible, consistent with a fluid slag should be used. Experimental studies indicate that operable slags of 0.1 - 0.2 basicity can be used.

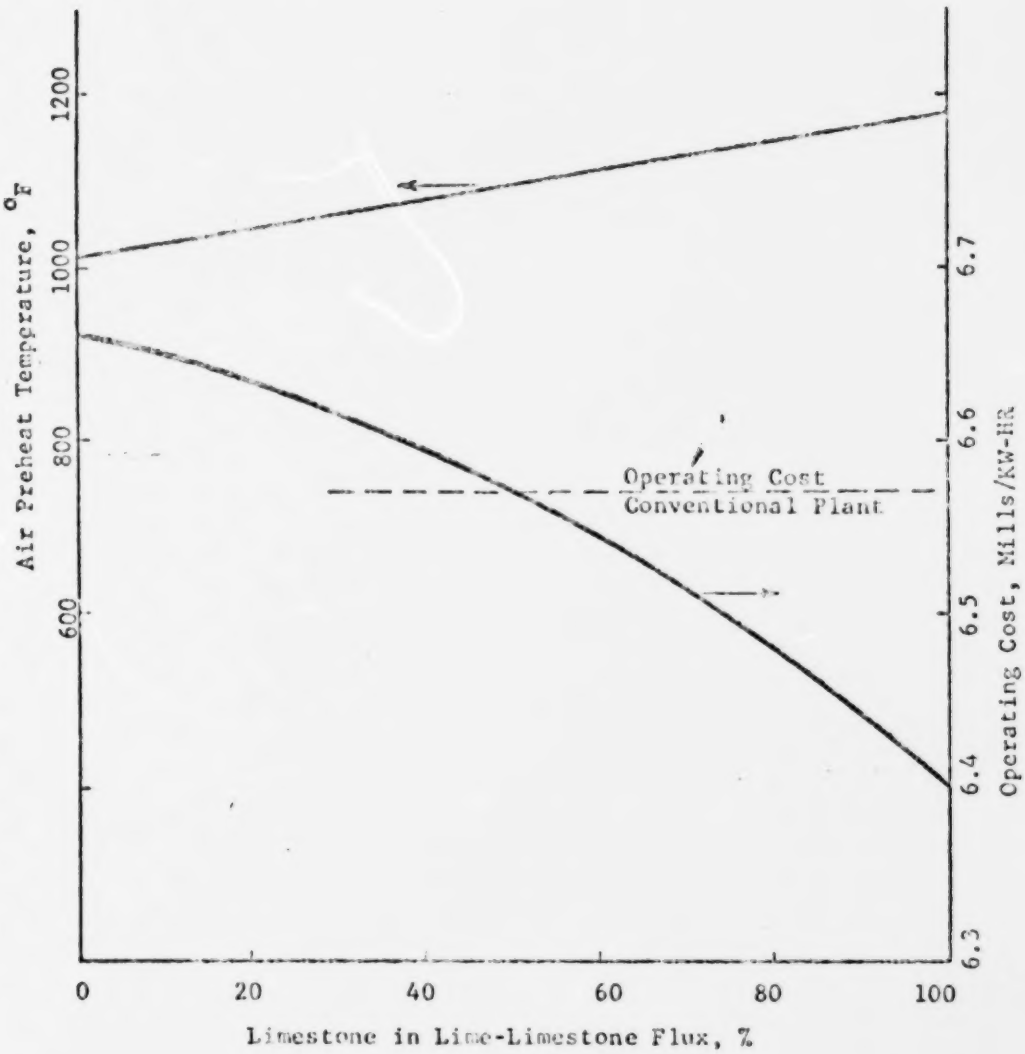
Perhaps the most important process parameter is the percent sulfur contained in the combustor slag. The air preheat temperature and operating cost for the process case under consideration are shown in Figure 8C, as a function of the percent sulfur in the slag. As seen, the process operating cost increases substantially when the percent sulfur in the slag is decreased below about 4 percent.

At about 4 percent sulfur in the slag, the operating cost of the Two-Stage Coal Combustion Power Station becomes equal to the conventional coal burning plant. At less than 4 percent sulfur, operating cost increases substantially. Fortunately, bench-scale laboratory experimentation has shown that slags containing 6 to 8 percent sulfur are sufficiently fluid for use in the combustor.

The main reason for the predominant economic effect of slag sulfur content lies in the fact that increased quantities of desulfurized slag

FIGURE 6C

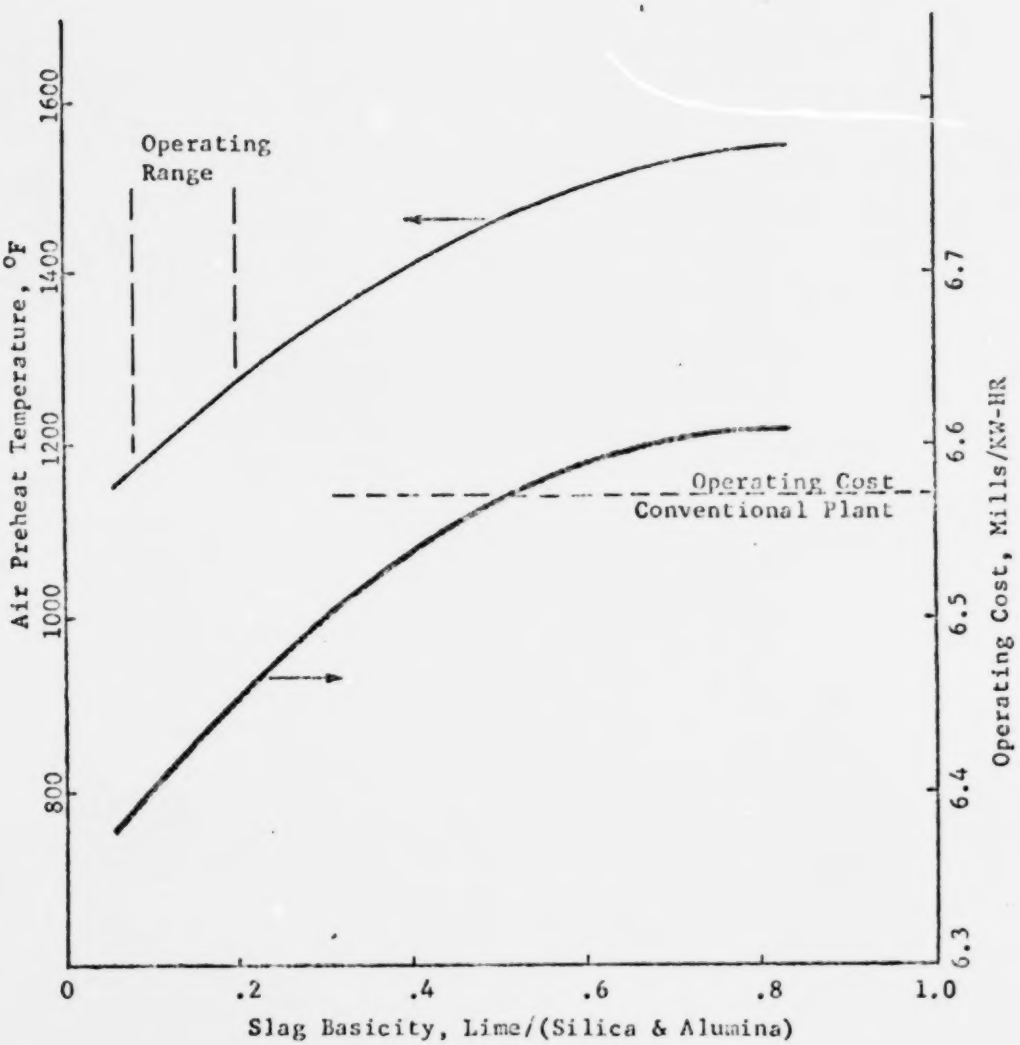
OPERATING COST/AIR PREHEAT TEMPERATURE VS
PERCENT LIMESTONE IN FLUX*



* 14.5% Ash - 1% Moisture Coal, 2500°F Combustor Temperature
.1 Basicity Slag, 1% Sulfur Slag

FIGURE 7C

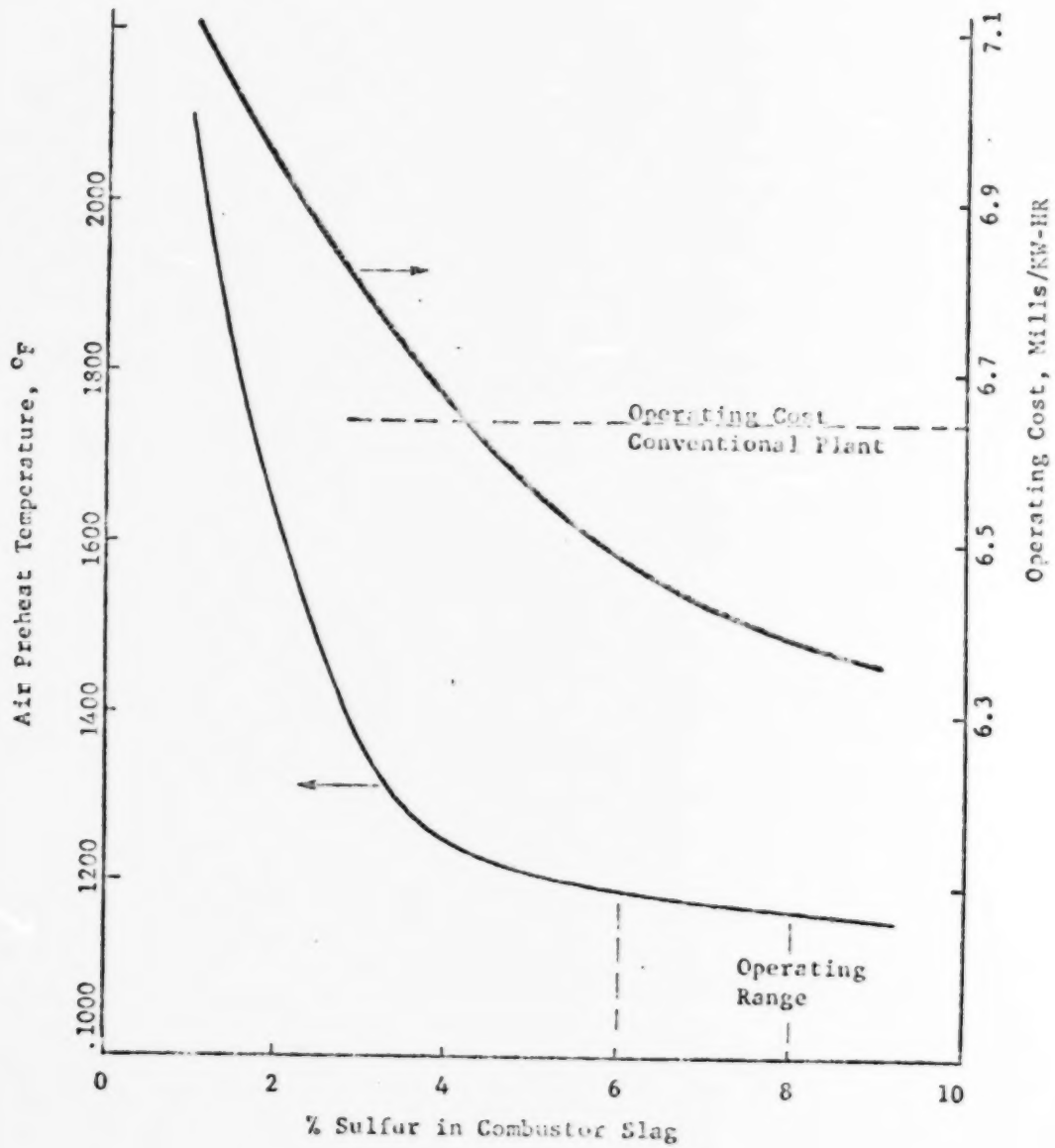
OPERATING COST/AIR PREHEAT TEMPERATURE
VS SLAG BASICITY*



* 14.5% Ash - 1% Moisture Coal, 2500°F Combustor Temperature
8% Sulfur in Slag, Limestone

FIGURE 8C

OPERATING COST/AIR PREHEAT TEMPERATURE VS
% SULFUR IN COMBUSTOR SLAG*



* 14.5% Ash - 1% Moisture Coal, 2500°F Combustor Temperature
.1 Slag Basicity, Limestone

must be recycled to the combustor and that both slag handling and slag desulfurization capital equipment costs are increased. Also more coal is required in the process to make up for the increased addition of desulfurized slag to the combustor which is at a temperature considerably lower than the combustor. In addition, more combustor offgas is consumed in the air preheating operation, since higher air temperatures are required (Figure 8C). This results in higher coal consumption to yield the fixed energy requirement of a 1000 MW power station.

Summary of Operating Ranges for Important Process Parameters

The process simulation - economic results determined above can be summarized as follows:

1. Low as well as high ash coals yield approximately the same capital and operating costs for the process. The air preheat temperature falls into the narrow range of 1000-1200°F for these coals. The process is, therefore, adaptable to a varying input coal composition as expected under normal power plant operation.

2. Coal moisture content should be as low as practical (1 to 2 percent).

3. The combustor operating temperature should be as low as possible (2500°F) consistent with a fluid slag operation.

4. Limestone rather than lime should be used to flux the coal ash--provided that the air preheat temperature is reasonable.

5. The basicity of the slag should be as low as possible to minimize the limestone requirement. A slag basicity of 0.1-0.2 should be used and based on experimental studies yields operable slags.

6. The sulfur content of the slag should be as high as possible. Slag sulfur contents of about 6 to 8 percent are preferred.

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